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# Environmental Effects of Oil Shale Mining and Processing. Part III: The Water Quality of Piceance Creek, Colorado, Prior to Oil Shale Processing

Colorado State Univ, Fort Collins

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# Environmental Effects of Oil Shale Mining and Processing

## Part III
## The Water Quality of Piceance Creek, Colorado, Prior to Oil Shale Processing

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Equilibrium calculations indicate that the natural conditions along Piceance Creek--in particular the alkaline pH range (7.5-8.5) and high carbonate alkalinity (300-800 mg $CaCO_3$/liter)-should limit the solubilities of most metals to levels below the standards for aquatic life.

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# ENVIRONMENTAL EFFECTS OF OIL SHALE MINING AND PROCESSING PART III - THE WATER QUALITY OF PICEANCE CREEK, COLORADO, PRIOR TO OIL SHALE PROCESSING

by

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## FOREWORD

This report describes the water quality of Piceance Creek, Colorado. Some of the first developments of the oil shale resource are anticipated in this area. The results should be useful as mining activity begins, to assess any changes in water quality as a result of mining activity.

Other reports in this series contain results of biological surveys.

Donald I. Mount, Ph.D.
Director
Environmental Research Laboratory-Duluth

## ABSTRACT

Water quality data have been collected at seven sites along Piceance Creek and at one site each along Stewart, Black Sulphur, and Yellow Creeks in the Piceance Basin, Colorado, during 1975-1977. Piceance, Stewart, and Yellow Creeks may be perturbed by oil shale industry activities on the two tracts, C-a and C-b, currently under development. The preoperational water quality is generally poor due to higher levels of dissolved solids (contributed to by calcium, magnesium, sodium, bicarbonate, sulfate, chloride, and potassium), manganese, and both dissolved and suspended iron. The quality of water along Piceance Creek also declined at sites farther downstream primarily due to influxes from groundwater aquifers in contact with soluble mineral beds. The highest concentrations of the most common ions were observed in June-August due to the combined effects of irrigation, evapotranspiration, and minimal surface runoff contributions.

The concentrations of aluminum, cadmium, chromium, lead, and boron were below the detection limits of the analysis method used. These were typically below the permissible levels set for aquatic life by factors of 5-10. The levels of copper, zinc, arsenic, selenium, and mercury were usually measurable but still below permissible levels. The levels of copper, zinc, and mercury were similar at all sites along Piceance Creek. The levels of arsenic, suspended iron, and manganese were highest at the downstream limit of sampling; the level of selenium showed the opposite trend.

Equilibrium calculations indicate that the natural conditions along Piceance Creek--in particular the alkaline pH range (7.5-8.5) and high carbonate alkalinity (300-800 mg $CaCO_3$/liter)--should limit the solubilities of most metals to levels below the criteria standards set in protection of aquatic life.

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# SECTION I

## INTRODUCTION

Concern has been raised over the possible environmental impacts of oil shale resource development in western Colorado. As part of a Federal prototype leasing program, the oil shale development rights to two tracts in Colorado have been acquired by several oil companies. As shown in Figure 1, these tracts, designated as C-a and C-b, are located in the northwestern part of the state, south and west of Meeker, Colorado. The focus in this report is on Piceance Creek, which is the major surface drainage of the area containing Tract C-b. Piceance Creek originates a few kilometers north of the town of Rio Blanco and flows west and north to the White River. Tract C-b is located immediately to the south of Piceance Creek, approximately 21 km northwest of Rio Blanco, between Stewart and Willow Creeks. The purpose of this study has been to establish the preoperational water chemistry characteristics along Piceance Creek before it is perturbed by mining activity. Results of studies on the identification and distribution of aquatic macroinvertebrates (Gray and Ward, 1978) and fishes (Goettl and Edde, 1978) in Piceance Creek have been reported separately. This report describes the chemical conditions found along Piceance Creek above, adjacent to, and below the C-b Lease Site.

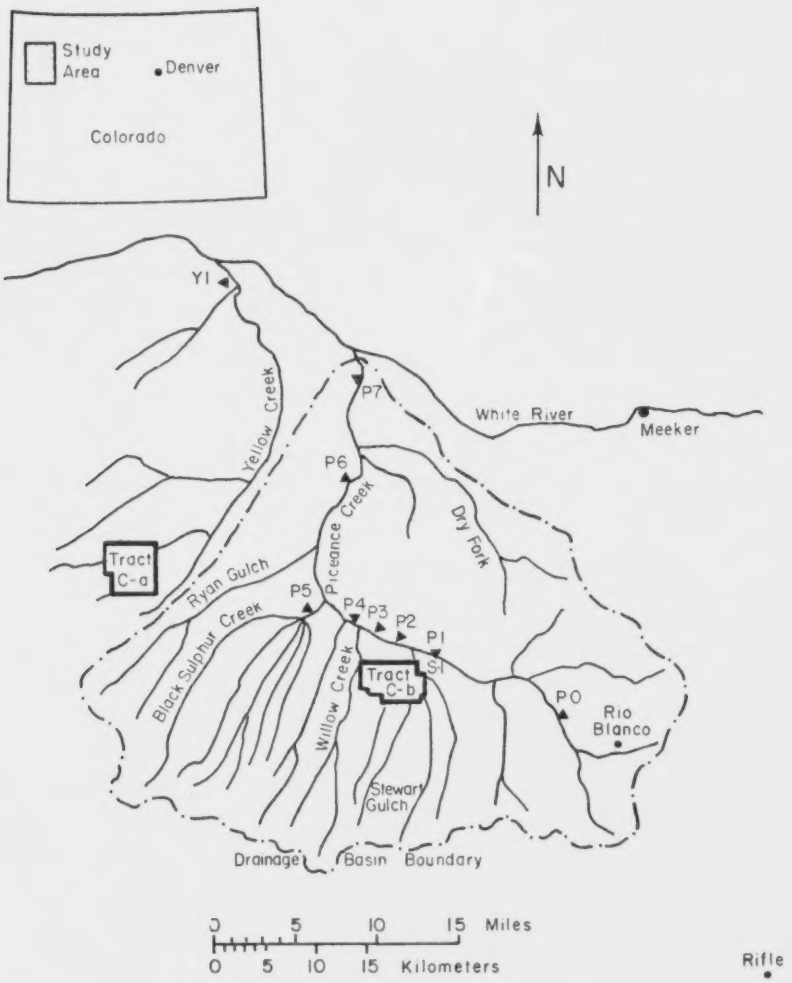


Figure 1. Location of the Piceance Basin and prototype oil shale Lease Tracts C-a and C-b (USGS State Base Map, Weeks et al., 1974) (—•— Piceance Creek drainage basin boundary, ▲ monitoring stations described in this report).

## SECTION II

## CONCLUSIONS

1. Water quality data have been collected at seven sites along Piceance Creek and at one site each on Stewart and Black Sulphur Creeks near their confluences with Piceance Creek, and on Yellow Creek near its confluence with the White River. These data are indicative of pre-operational water quality conditions in the Piceance drainage basin.

2. Along Piceance Creek, significant increases in dissolved solids primarily due to increases in magnesium, sodium, bicarbonate, and sulfate occur at successive downstream sites. These increases are indicative of fairly large influxes of poor quality groundwaters into the stream.

3. The spatial and temporal distribution curves for the common ions all show a common pattern. The highest concentrations are observed at the farthest downstream site in the summer season (June-August) due to the combined effects of irrigation, evapotranspiration, and subsurface inflow contributions.

4. The level of dissolved solids is above the permissible level of 500 mg/liter (U.S. Public Health Service, 1962) at all sites adjacent to or below Tract C-b.

5. The levels of trace elements tend to be low at all sites during all seasons. The levels of aluminum, cadmium, chromium, lead, and boron were all below the detection limits, which are below the permissible levels set for aquatic life by factors of 10-20 (U.S. Environmental Protection Agency, 1977). The levels of copper, zinc, arsenic, selenium, and mercury were usually detectable but still below the safe drinking water levels. Levels above the limits set by the U.S. Public Health Service (1962) at sites both above and below Tract C-b were observed for manganese (10% frequency), dissolved iron (5% frequency), suspended iron (47% frequency), and total iron (52% frequency).

6. Along Piceance Creek, the levels of suspended iron, arsenic, and manganese are higher at the downstream limit of sampling than at the upstream limit of sampling. These increases can be explained on the basis of the larger quantities of these elements in the groundwater aquifers, which contribute more water to the stream at lower elevations.

7. The level of selenium is higher at the upper limit of the stream than at the lower. This is unexpected since larger quantities of selenium are found in the groundwater aquifers than in the alluvial aquifer. This suggests that selenium may be removed from the stream by a physical, chemical, or biological process that is inoperative for any of the other trace elements analyzed.

8. Equilibrium calculations, using the common precipitating anions to define representative conditions, indicate that the levels of the trace metals may be increased; but that except for manganese, their concentrations should remain below the USPHS permissible levels. The naturally occurring pH along Piceance Creek (7.5-8.5) is in fact near the optimum level for maintaining low levels of many metal ions through precipitation control. Since the waters, due to the high levels of bicarbonate ion, also have significant buffer capacities for both acid and base, these conditions are likely to persist in the face of perturbations by the development of the oil shale industry unless such perturbations involve major influxes of acid or base material and/or metal complexing agents.

## SECTION III

## RECOMMENDATIONS

The present data indicate the water quality characteristics of Piceance Creek prior to the initiation of oil shale development. They are also indicative of the existence of sites where groundwater breakthrough to the surface is more prominent. It is recommended that these data be considered as preoperational references and that monitoring of Piceance Creek be continued as oil shale development evolves. It is also recommended that this monitoring program focus on the springs associated with the C-b tract along Stewart and Willow Creeks, as well as the fault breakthrough near Black Sulfur Creek, as those points are most likely to reflect early impacts on water quality because of the adoption of the *in situ* and/or modified *in situ* retorting technology.

## SECTION IV

## DESCRIPTION OF THE STUDY AREA

### PHYSICAL DESCRIPTION

The Piceance Creek Basin is characterized by north to northeast trending ridges and valleys (Gray and Ward, 1978). Elevations near the Lease tracts range from 2000 to 2350 m with local reliefs of 60 to 180 m. The basin is classified as semiarid since total annual precipitation is only 30 to 46 cm. The natural vegetation of the area is typical of the Great Basin desert. Big sagebrush is dominant in valleys and on slopes, while pinyon-juniper woodland dominates on ridge tops. Hay is grown on irrigated land in the stream valleys and some shrubland has been cleared (chained) to promote grassland for grazing.

### GEOLOGY

As described by Weeks et al. (1974), this area has been the site of considerable sediment deposition from a huge lake which covered much of northwestern Colorado during the Eocene epoch. In some areas, clay and finely grained sediment deposits were 1067 m thick. Organic-rich layers derived from plant and animal life were also deposited and then covered by newer sand, silt, and clay sediments which eventually filled the lake. The weight of these newer sediments consolidated the earlier mineral deposits into sandstone, shale, and marlstone and the organic-rich material into the solid hydrocarbon called kerogen. It is the marlstone, rich in kerogen, that is commonly called oil shale. The resulting strata are shown in Figure 2; these are representative of the strata of Tract C-b.

The oil shale strata are now classified as part of the Parachute Creek Member of the Green River Formation. Of greatest commercial interest is the Mahogany zone which ranges in thickness from 30 to 61 m and lies near the upper extreme of this member. It is overlain by about 150 m of marlstone of the Parachute Creek Member and 0 to 365 m of sandstone, siltstone, and marlstone that are part of the Uinta formation. At Tract C-b, the Mahogany zone is about 275 m below the surface (Donnel, 1961).

### HYDROLOGY

Snowmelt in March or April produces the highest streamflow and recharges the alluvium. Most rainfall is lost by evapotranspiration except during intense and usually localized thunderstorms; hence by July, streamflow is

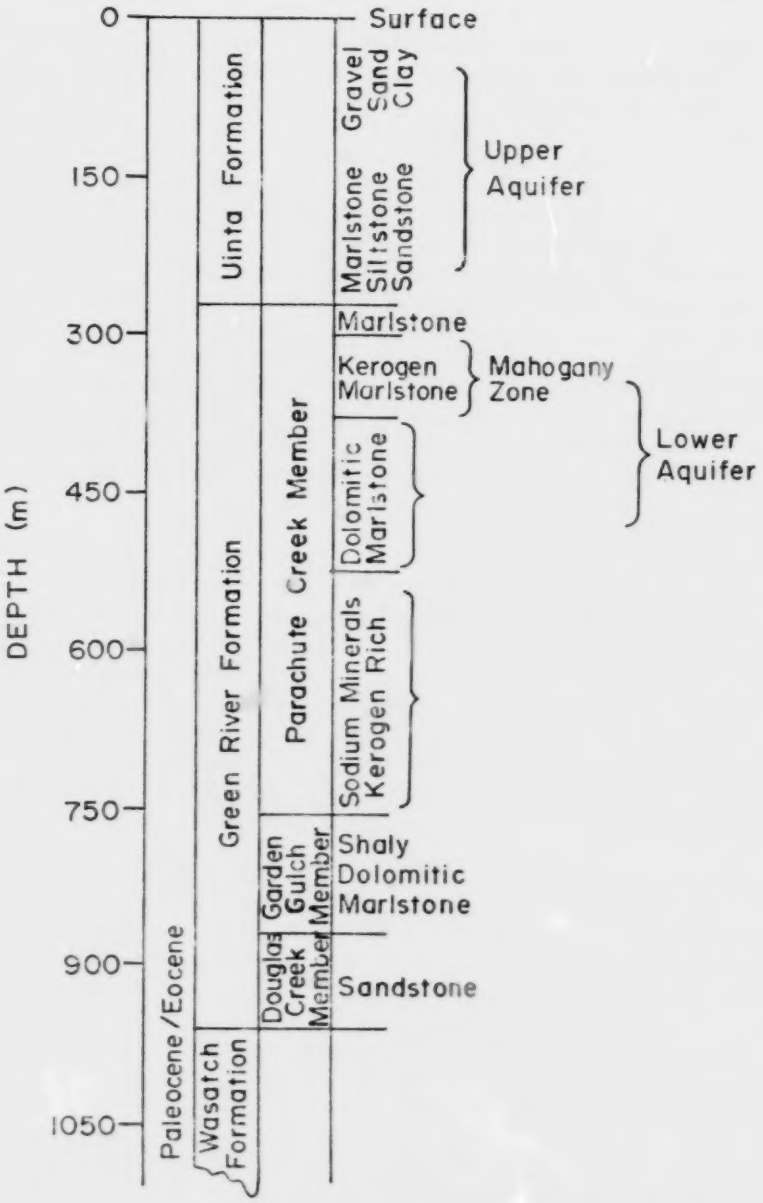


Figure 2. Generalized columnar section of the Piceance Basin including location of aquifers (Donnel, 1961).

due almost entirely to groundwater discharge. Streamflow characteristics are also altered and variable between mid-March and early November due to irrigation diversions. The amount of water diverted depends on weather, crop types, and season.

The groundwater conditions associated with the Piceance Creek drainage area have been thoroughly characterized, with respect to both hydrologic and chemical parameters, by Weeks et al. (1974). Their results will be summarized here for the convenience of the reader. Piceance Creek is underlain by three aquifers: an alluvial aquifer confined largely to valley bottoms along creeks, and two groundwater aquifers separated by the Mahogany zone. Recharge of the groundwater aquifers occurs most effectively at altitudes above 2100 m where the snowpack thaws slowly enough to infiltrate, increase soil moisture content to capacity, and thence percolate into the saturated zone. Faults may be the most effective pathway for transfer of water from the upper to the lower aquifer (Weeks et al., 1974). Both the upper and lower aquifers contribute to stream recharge; contributions from the lower aquifer are most significant along the lower portions of the stream. Figure 3 is a diagram of a geohydrologic section through the drainage basin (Weeks et al., 1974); it shows how the variations in altitude within the basin direct water flow from both aquifers toward the low point--i.e., Piceance Creek.

The general water quality characters of all three aquifers are summarized in Table 1. These data demonstrate that the water quality of the alluvial and upper aquifers is comparable but that the water quality of the lower aquifer is significantly lower. The levels of several constituents in the lower aquifer are much higher: dissolved solids concentrations in the upper aquifer range from 500-2000 mg/liter while those in the lower aquifer vary from 1000 to 30,000 mg/liter (Weeks et al., 1974). Large deposits of nahcolite (sodium bicarbonate) and halite (sodium chloride) underlie much of Piceance Creek and are largely responsible for the high levels of alkalinity, sodium, and chloride in the various aquifers.

The aquifers have also been analyzed for trace elements (Weeks and Welder, 1964). The results summarized in Table 2 indicate that the concentrations of most trace constituents are significantly higher in the lower aquifer. The lower aquifer is found to have measurable levels of aluminum, arsenic, barium, boron, iron, lead, lithium, manganese, molybdenum, selenium, and strontium. In particular, the levels of boron, barium, and lithium are frequently observed at levels above those set by USPHS (1962) (barium = 1000 µg/liter) or above levels cited by Hem (1970) as toxic to plants (boron, 3000 µg/liter and lithium 5000 µg/liter).

The presence of several aquifers, irrigation diversions, and high evapotranspiration demands results in a complicated water budget for the area. This may be complicated further by two factors. First, the oil shale industry may require significant amounts of water. Second, the Mahogany zone, which currently separates the two groundwater aquifers, will be altered and/or removed (perhaps drastically). These perturbations may therefore affect both hydrologic and water quality parameters of the Piceance Creek drainage area. The complicated nature of flow patterns (Figure 3)

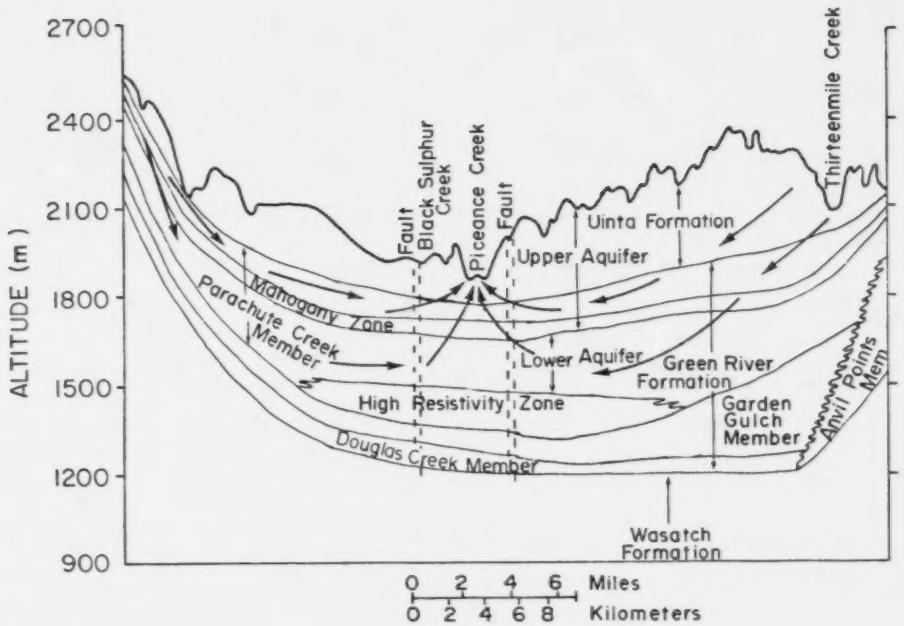


Figure 3. Geohydrologic section through the Piceance Creek Basin showing the relation of the aquifers to the Green River and Uinta Formation. [Arrows indicate direction of water movement (Weeks et al., 1974)].

TABLE 1. AVERAGE CONCENTRATIONS (IN MEQ/LITER) OF CHEMICAL CONSTITUENTS IN GROUNDWATER AQUIFERS ASSOCIATED WITH TRACT C-b (WEEKS ET AL. 1974)

| Water quality parameter | Alluvial aquifer | Upper aquifer | Lower aquifer |
|---|---|---|---|
| K | 0.08 | 0.04 | 0.3 |
| Na | 20.00 | 8.00 | 175.0 |
| Ca | 4.00 | 3.00 | 0.3 |
| $HCO_3$ | 7.00 | 5.00 | 0.8 |
| Cl | 20.00 | 9.00 | 150.0 |
| $SO_4$ | 1.00 | 0.50 | 20.0 |
| F | 10.00 | 7.00 | 1.9 |
| Mg | 1.80 | 0.08 | 1.8 |

TABLE 2. TRACE ELEMENT ANALYSES (IN µG/LITER) FROM WATER WELLS IN THE PICEANCE DRAINAGE BASIN (WEEKS AND WELDER, 1964; WEEKS ET AL., 1974)

| Element | Upper aquifer | | Lower aquifer | |
|---|---|---|---|---|
| | Tract C-b | Tract C-a | Tract C-b | Tract C-a |
| Aluminum | --[a] | -- | 0 | 0 |
| Arsenic | 3 | 2 | 70 | 17 |
| Boron | -- | 5,600 | 250,000 | 5,500 |
| Dissolved iron | -- | 190 | 3,300 | -- |
| Lead | -- | <50 | -- | 300 |
| Manganese | -- | 10 | 200 | 30 |
| Selenium | -- | 5 | 40 | -- |

[a] Dashed lines indicate no data available.

makes the prediction of mining activity impact difficult. It is therefore particularly important to characterize the premining water quality conditions so that perturbations due to the oil shale related activities can be rapidly identified if and/or when they occur. This report summarizes these conditions.

## SECTION V

## DESCRIPTION OF THE MONITORING STATIONS

The locations of the monitor sites of the present study are shown in Figure 4 and described in more detail in Table 3. Stations P0 and P1 are located upstream of Tract C-b and thus serve as reference points. Stations P2-P4 are located on sites which reflect inflow from streams (Stewart and Willow Creeks) and aquifers draining the C-b area. Site S1 on Stewart Creek is indicative of its possible impacts on Piceance Creek. Sites P6 and P7 are located about 10 miles farther downstream near the confluence with the White River. The section of the creek between P4 and P6 is recipient of increasingly larger groundwater inflows from springs. Moreover, Weeks et al. (1974) believed that the lower aquifer discharges directly into the alluvial aquifer near site P7 so that water quality changes occurring between P6 and P7 should reflect this. Site P5 is located on Black Sulphur Creek just prior to its confluence with Piceance Creek; the analysis reflects only the characteristics of the former but is indicative of its possible impact on the latter. Finally, the Y1 station reflects the overall characteristics of the inflow from the Tract C-a watershed. The locations of these stations coincide with those of the macroinvertebrate study (Gray and Ward, 1978) and are such that an overview of the preoperational water quality characteristics and inflow contributions can be obtained.

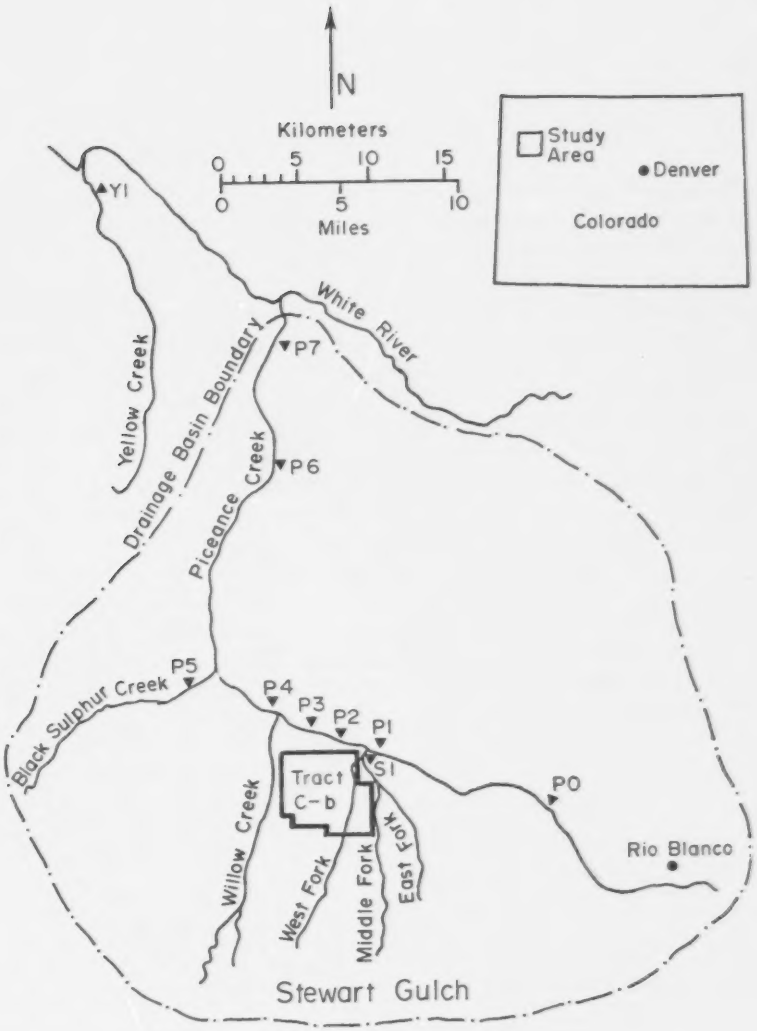


Figure 4. Location map of the water quality monitoring stations and drainage basin boundary of the study area (see Table 3 for description).

TABLE 3. DESCRIPTION OF THE WATER QUALITY SAMPLING STATIONS[a/]

| | Station number | | | | | |
|---|---|---|---|---|---|---|
| | Piceance Creek | Stewart Creek | Black Sulphur Creek | Yellow Creek | Elevation | Site description |
| | P0 | | | | 2103 m (6900 ft) | Piceance Creek about 8.0 km downstream from Rio Blanco |
| | P1 | | | | 1987 m (6520 ft) | Piceance Creek, 2.5 km upstream from confluence with Stewart Creek |
| | | S1 | | | 1999 m (6560 ft) | Stewart Creek 50 m above confluence from Piceance Creek |
| | P2 | | | | 1975 m (6480 ft) | Piceance Creek about 300 m downstream from confluence with Stewart Creek |
| | P3 | | | | 1963 m (6440 ft) | Piceance Creek 4.1 km upstream from confluence with Willow Creek |
| downstream | P4 | | | | 1902 m (6240 ft) | Piceance Creek about 100 m downstream from confluence with Willow Creek |
| | | | P5 | | 1902 m (6240 ft) | Black Sulphur Creek 2.6 km upstream from confluence with Piceance Creek |
| | P6 | | | | 1798 m (5900 ft) | Piceance Creek 1.0 km upstream from confluence with Dry Fork |
| | P7 | | | | 1749 m (5740 ft) | Piceance Creek 2.5 km upstream from confluence with White River |
| | | | | Y1 | 1689 m (5540 ft) | Yellow Creek 1.5 km upstream from confluence with White River and 80 m upstream from USGS gauging station |

[a/] Collections at all sites were carried out monthly from October 1975 through March 1977.

## SECTION VI

## METHODS AND PROCEDURES

Water samples were collected at each sampling station on a monthly basis. These were preserved according to the recommended procedures described in the EPA manual on water analysis and analyzed by the standard procedures given therein (U.S. Environmental Protection Agency, 1974). The data obtained were keypunched and placed on permanent tape file in the university computer system so that they could be summarized and evaluated via any of several available procedures, and are available in a summary compilation (Skogerboe et al., 1978).

An analytical quality assurance program was maintained throughout the term of this project. This included: (1) submission of the same samples to the analytical lab under different numerical designations to obtain precision estimates; (2) running reference water samples from the U.S.G.S. (using a designation system which disguised the fact that they were reference samples) to obtain accuracy estimates and; (3) cross checking analyses by using spike-recovery methods. Approximately 3-4% of all samples analyzed were actually check samples of the above types. The overall conclusions drawn from these quality assurance checks was that the analyses are typically accurate to ±10% of the stated value; certain types of measurements, e.g., pH and specific conductivity were found to be accurate to better than ±5%.

## SECTION VII

## RESULTS AND DISCUSSION

Sampling was carried out at the sites described above from October 1975 through March 1977. The results of the water quality analyses are summarized for all parameters on a monthly basis in a summary compilation available upon request at cost of reproduction (Skogerboe et al., 1978). An overview evaluation of these data is presented in general terms below for the convevenience of the reader. The following discussion is segmented into consideration of the most commonly measured parameters and the trace metals.

### GROSS PARAMETERS AND COMMON IONS

In developing an overview of the present water quality characteristics of the area and the impacts of inflow from associated streams and aquifers, it is expedient to consider the dissolved solids data in relation to the monitor network as a general indication of similarities and differences. Figure 5 presents a summary of the maximum, minimum, and average dissolved solids concentrations along Piceance Creek. Notable features of these data include the following:

1. The dissolved solids concentrations consistently exceed 500 mg/liter at all sites below P0.

2. The differences between levels at P0 and P1 generally reflect the effects of both aquifer inflow and irrigation return flow in that segment of the stream.

3. Changes observed between P1 and P2 and P3 and P4 reflect the inflows from Stewart and Willow Creeks, respectively. The water quality characteristics of Stewart Creek are very comparable to those observed at P2 and P3. In addition, there are relatively minor changes in the levels of the parameters between P2 and P4. Thus, the inflows of Stewart and Willow Creeks have relatively minor effects on the water quality parameters along this section of the stream. In view of this, averages of the parameter concentration levels for sites P2-P4 may be used in the generalized overview analysis.

4. Differences between P4 and P6 partially reflect the input of Black Sulphur Creek which has generally higher levels of most constituents than those observed at P4. This may be due to upwelling from the lower aquifer through the fault associated with Black Sulphur Creek (Figure 3).

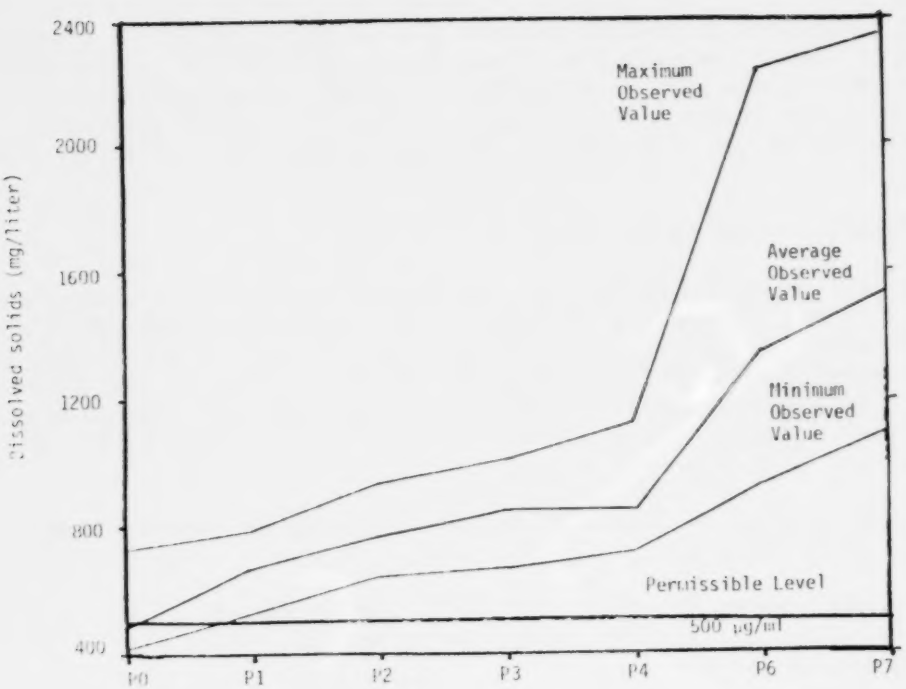


Figure 5. Plot of minimum, maximum, and average dissolved solids measured at each site along Piceance Creek. (Permissible level from U.S. Public Health Service, 1962.)

5. The concentration increases between P6 and P7 reflect the discharge of water from the lower aquifer (Figure 3) into the stream (Weeks et al., 1974).

In essence, evaluation of the results based on these general features provides general indications of the contributions to streamflow (and their concomitant effects on the water quality parameters) by groundwater and irrigation return flows.

Consideration of streamflow, climatological data, and local agricultural practices has also been used to choose the following seasonal groupings on a general basis.

1. The months of September-November represent a dry period with below freezing nights. Although irrigation along the creek is often continued into November, losses by evapotranspiration are generally low.

2. During December-February the streamflow is at a minimum and no irrigation is carried out. Most snowfall occurs during this period, but runoff due to snowmelt is at a minimum.

3. March-May are the months of maximum snowmelt runoff at the elevations associated with the Lease sites. Snowmelt from higher elevations upstream may extend into June. Irrigation is often resumed by April.

4. Evapotranspiration demands and irrigation requirements are generally the greatest during June-August. Streamflow gradually decreases during this period as snowmelt at higher elevations is completed.

These seasonal time groupings have been used in the present overview analysis as a further means of differentiating between average effects associated with the different sources of water quality impacts.

Finally, it should be noted that the data for the sites not directly on Piceance Creek, i.e., S1, P5, and Y1, agree well with results reported by the U.S. Geological Survey (Weeks et al., 1974; Weeks and Welder, 1964) as do the on-stream results. The concentration levels of the off-Piceance sites are consistent with their elevations and their locations relative to the characteristics of the contributing aquifers and associated mineral deposits. Although the data for these three sites (S1, P5, and Y1) are not specifically discussed below, the results for S1 and Y1 (Skogerboe et al., 1978) will serve as preoperational references for Stewart and Yellow Creeks, respectively. Stewart Creek will likely be perturbed by oil shale development activities at Tract C-b while Yellow Creek may be affected by activities on Tract C-a. Further, it is possible that Black Sulphur Creek (P5) may not receive waters associated with either Lease tract. Due to the topography of the region, the aquifers contributing to this creek do not appear to be directly involved with the shale development sites. As a result, it is possible that the present data could be used in combination with future data to estimate the natural variations in water quality characteristics in the western portions of the watershed and thereby serve as a comparative reference for variations occurring on streams more likely to be impacted.

On the basis of the above discussion, the average concentrations of the common water quality parameters have been determined and summarized in spatial and temporal plots to provide a general overview. Consideration of Figure 6, which summarizes the dissolved solids results, indicates the following:

1. Upstream of P6, the dissolved solids concentrations are relatively constant within a season at each individual site. The increasing trend from P0 to P4 is small compared to increases below P4. The similarities in these trends from season-to-season imply that irrigation return flow does not have a major impact (compare June-August with December-February).

2. Below P4, the inflow of ground waters through springs results in sharper increases in dissolved solids and greater variations in seasonal fluctuations. The occurrence of a maximum level of dissolved solids during the June-August period reflects increases in the relative contributions of subsurface waters to streamflow coupled with higher evapotranspiration demands and increased irrigation return flow. The combined effects of these may be approximated by comparison with the December-February period during which all three contributing factors are at minima.

The general trends observed for dissolved solids recur for most of the common water quality parameters. Examination of the graphs of these (Figures 7-16) leads to a general conclusion. The dissolved solids increases are due primarily to increases in the levels of sodium, bicarbonate, magnesium, sulfate, and (to a lesser extent) chloride. On the other hand, the level of calcium is lower at P7 than at upstream sites. These changes, which are generally most prominent between P6 and P7, reflect in particular the inflow of lower quality water from the lower aquifer (Table 1 and Figure 3). They may also reflect the removal of dissolved calcium by precipitation as the carbonate of the stream increases (compare Figures 8 and 11). Finally, the data suggest the predominance of equilibria associated with certain types of minerals, e.g., nahcolite ($NaHCO_3$), halite (NaCl), epsomite ($MgSO_4$), and gypsum ($CaSO_4$) (Weeks et al., 1974). The fact that the pH of the stream is quite constant on both temporal and spatial bases testifies to the general predominance of a pH-controlling set of equilibria related to the general mineralization of the region. These common characteristics must also directly or indirectly influence the concentrations of trace metals.

## HEAVY METALS

The levels of most trace elements were low at all sites during all seasons. The levels of aluminum, cadmium, chromium, lead, and boron were all below the detection limits, which are generally below the permissible levels for aquatic life [(U.S. Environmental Protection Agency, 1977) see Table 6] by factors of 10-20. The levels of copper, zinc, arsenic, selenium, and mercury were usually detectable but still below the permissible levels for aquatic life (U.S. Environmental Protection Agency, 1977). Levels above these were observed only for suspended and dissolved iron and for manganese. These data are summarized in Table 4. Data obtained for detectable elements

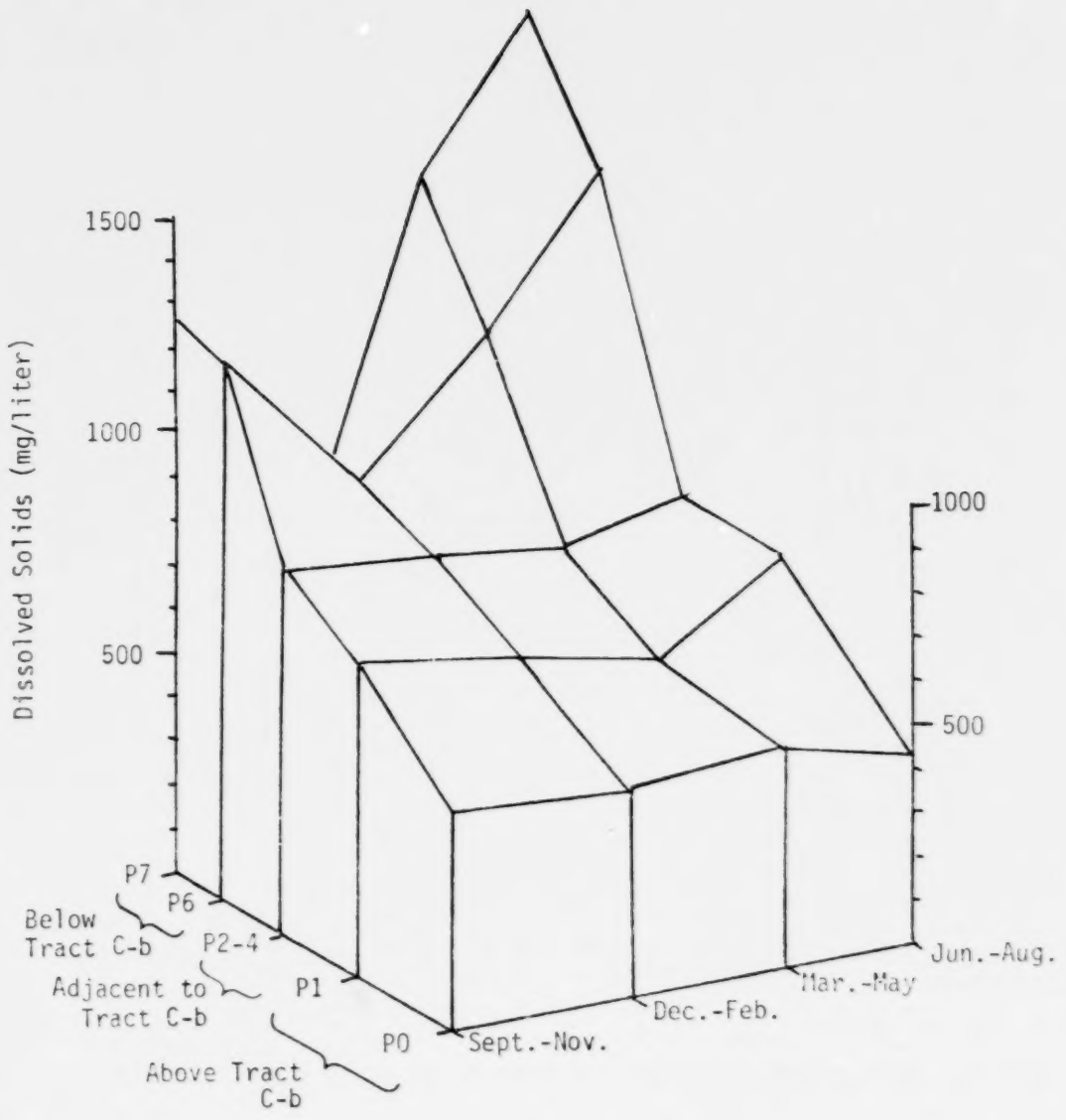


Figure 6. Spatial and temporal distribution of dissolved solids concentration.

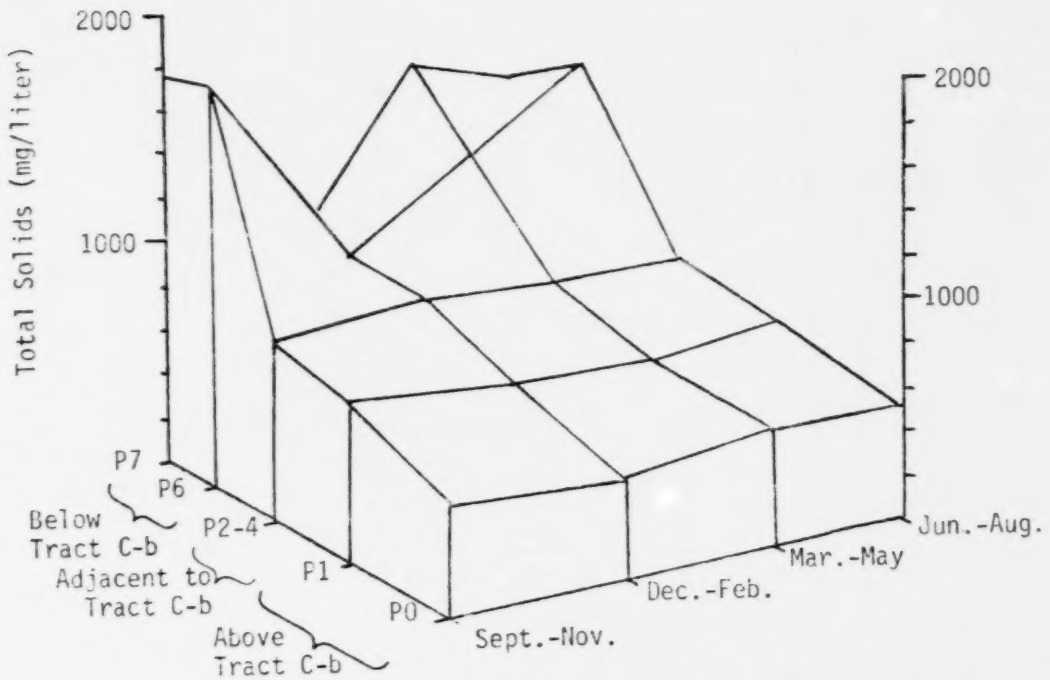


Figure 7. Spatial and temporal distribution of total solids concentration.

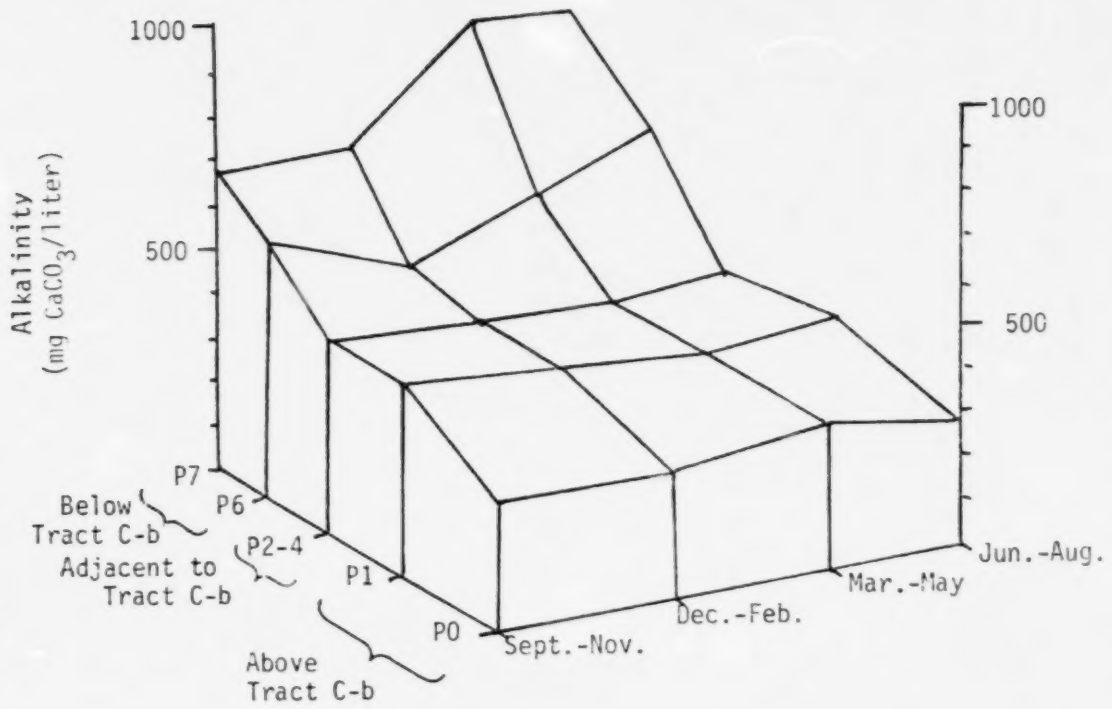


Figure 8. Spatial and temporal distribution of alkalinity.

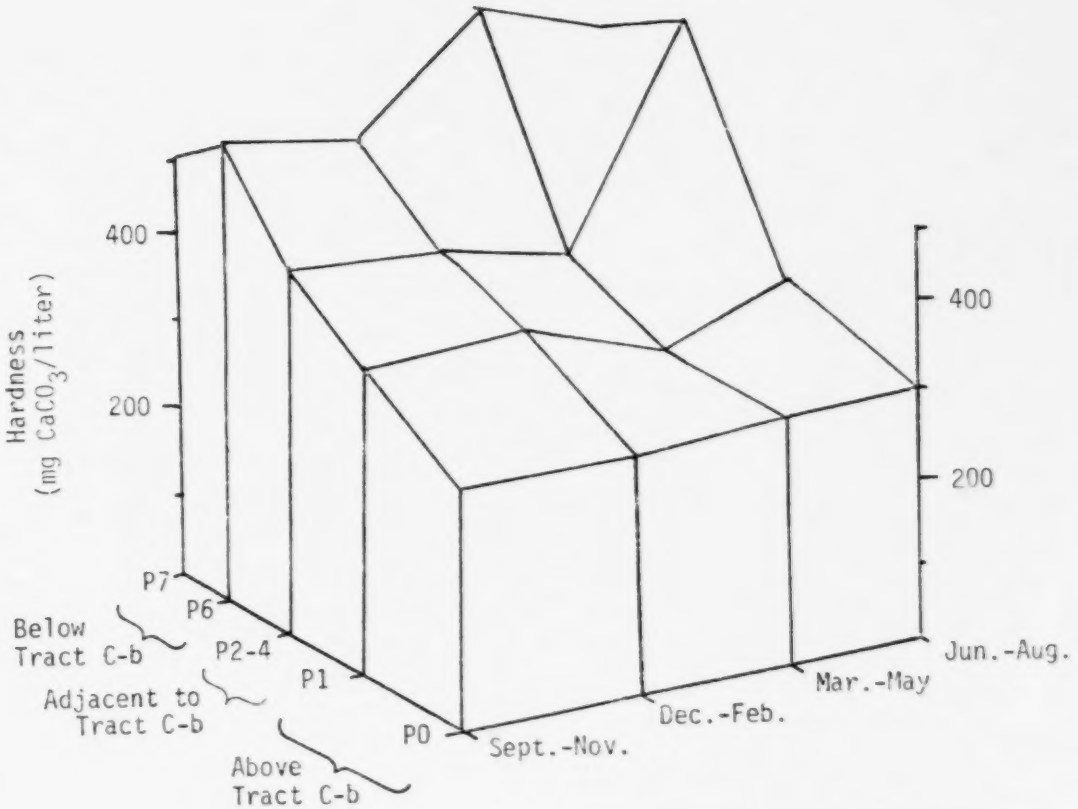


Figure 9. Spatial and temporal distribution of hardness.

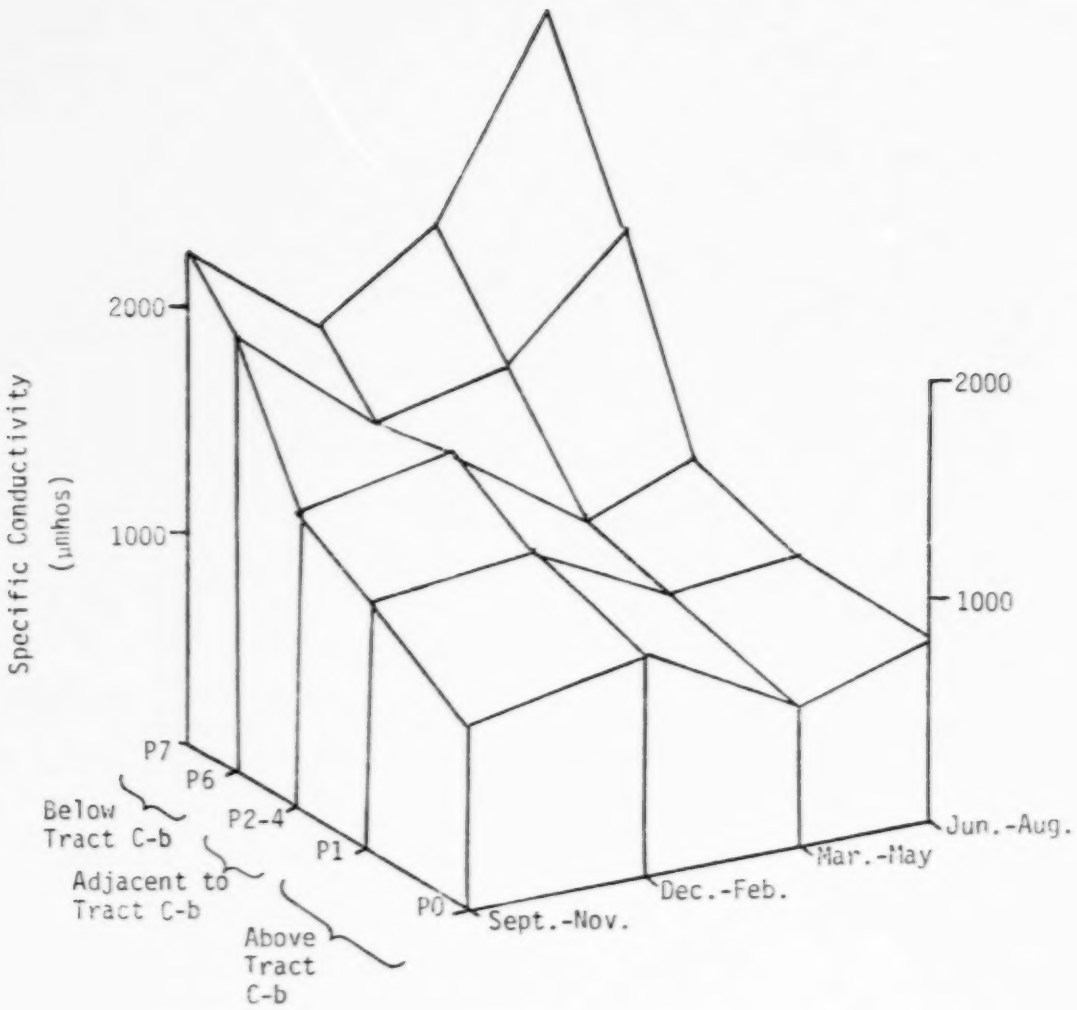


Figure 10. Spatial and temporal distribution of specific conductivity.

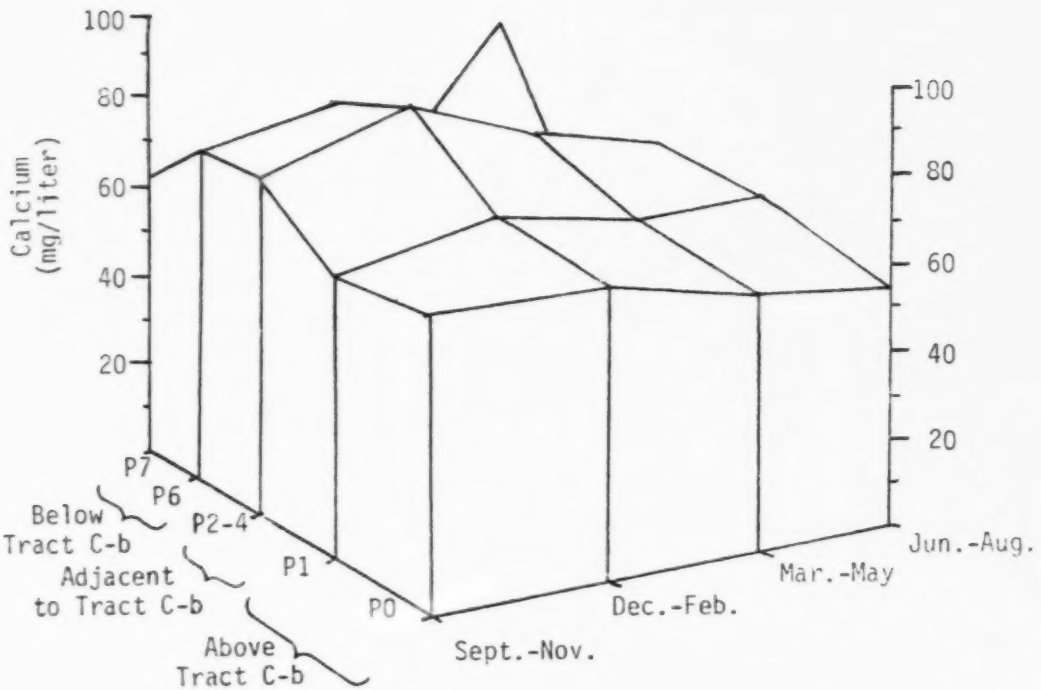


Figure 11. Spatial and temporal distribution of calcium concentration.

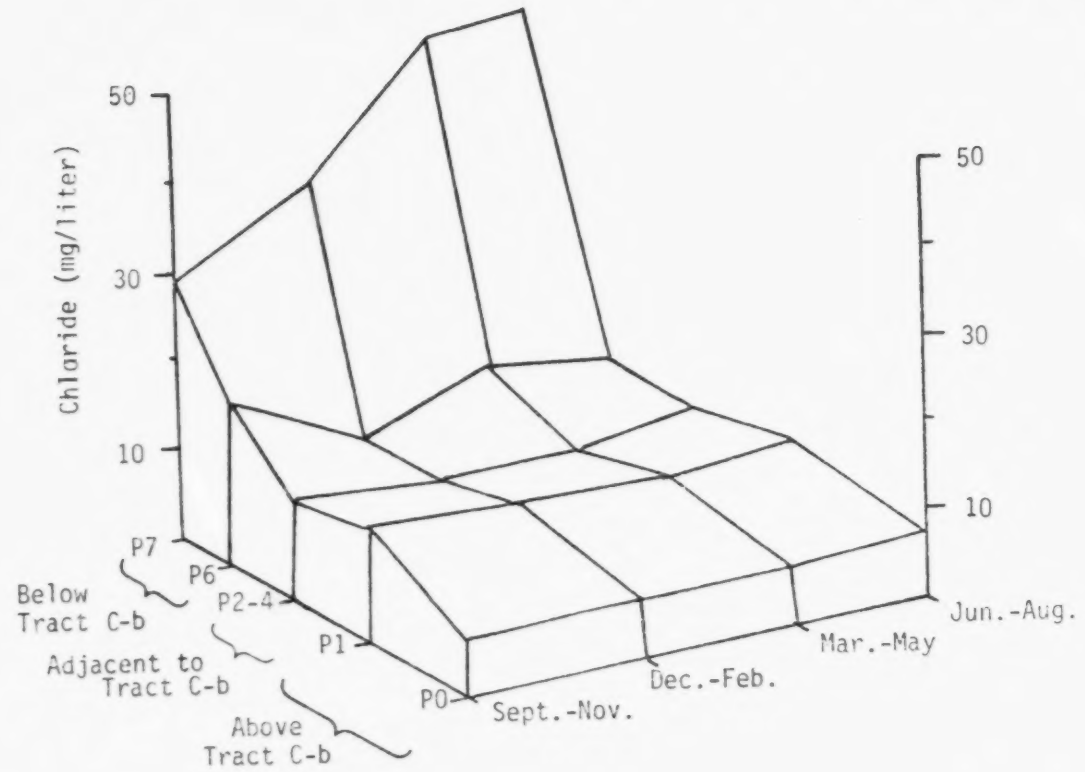


Figure 12. Spatial and temporal distribution of chloride concentration.

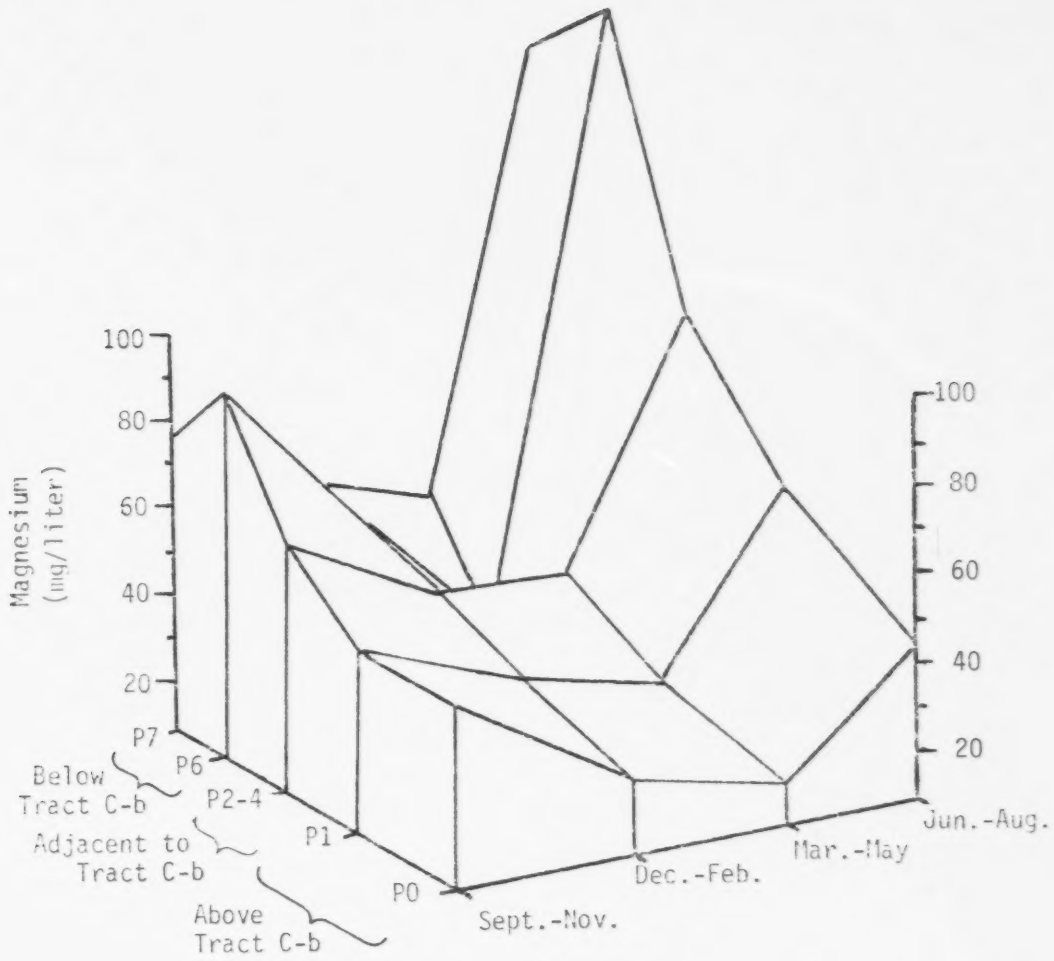


Figure 13. Spatial and temporal distribution of magnesium concentration.

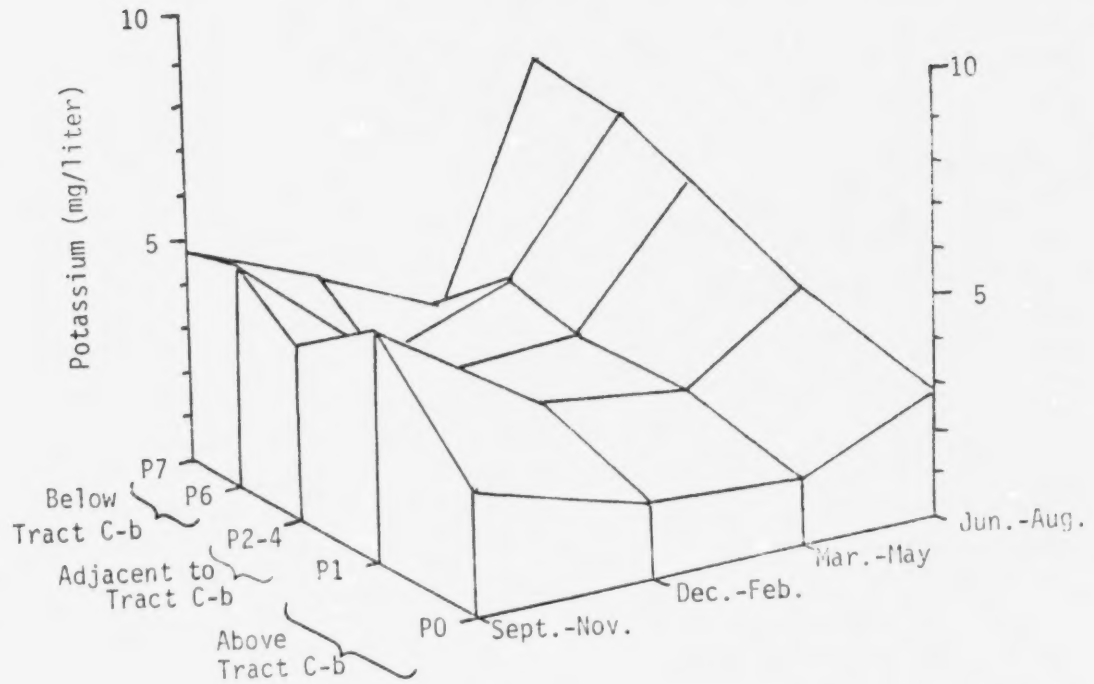


Figure 14. Spatial and temporal distribution of potassium concentration.

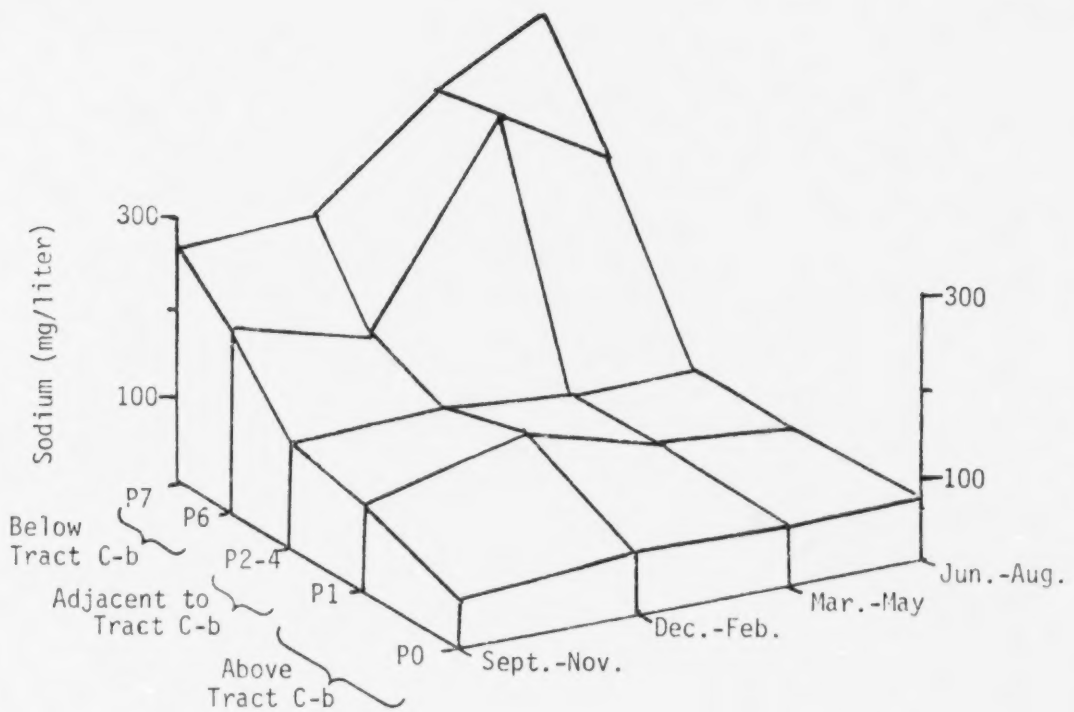


Figure 15. Spatial and temporal distribution of sodium concentration.

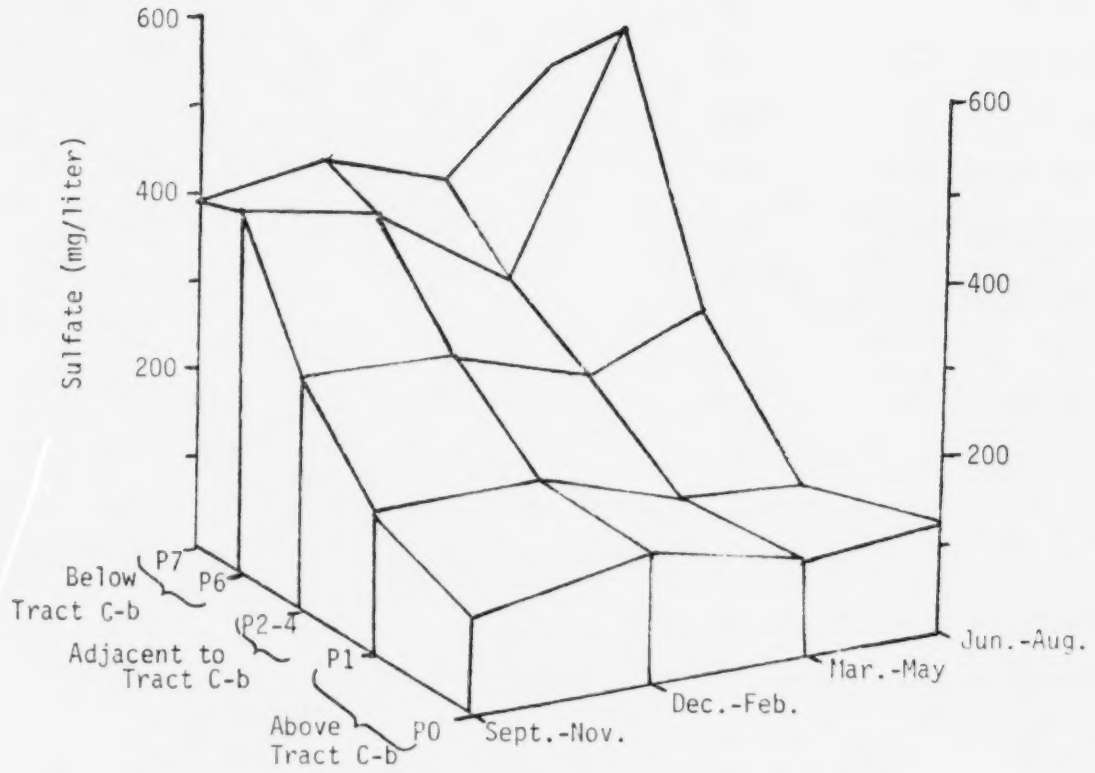


Figure 16. Spatial and temporal distribution of sulfate concentration.

TABLE 4. FREQUENCY WITH WHICH TRACE CONSTITUENT LEVELS WERE ABOVE USPHS LIMITS FOR SAFE DRINKING WATER

| Constituent | USPHS limit (µg/liter)[a] | Frequency observed above USPHS limit (%) | Number of times detectable[b] |
|---|---|---|---|
| Arsenic | 50 | 0 | 60 |
| Boron | 3000 | 0 | 38 |
| Cadmium | 10 | 0 | 110 |
| Chromium | 50 | 0 | 100 |
| Copper | 1000 | 0 | 110 |
| Iron (dissolved) | 300 | 5.5 | 110 |
| Iron (suspended) | 300 | 47.0 | 125 |
| Iron (total) | 300 | 52.0 | 107 |
| Lead | 50 | 0 | 110 |
| Manganese | 50 | 10.0 | 110 |
| Selenium | 10 | 0 | 60 |
| Zinc | 5000 | 0 | 109 |

[a] U.S. Public Health Service (1962).

[b] Total sample analyses = 18 mo. × 10 samples/mo. = 180

at sites P0 (farthest upstream) and P7 (farthest downstream) are given in Figure 17. The bars indicate the range of concentrations observed for each element over the sampling period. If an element was not always detectable (copper, dissolved iron, mercury, manganese, and zinc), the lower end of the bar indicates the detection limit; for the other elements (selenium, arsenic, and suspended iron) the lower end indicates the minimum observed value. An average concentration was also computed; for elements in which some concentrations were below the detection limit, the detection limit was taken as an estimate of the actual concentration present. As a result, the averages--indicated by the -☆- symbol on each bar--are upper limit estimates of actual values. The percentage value given at the top of each bar indicates the percentage of samples for which the element concentration was above the indicated detection limit. This treatment results in a greater overestimation of the average value when an element is detected fewer times; however, approximate information may still be obtained from such an estimate.

The data in Figure 17 indicate that the concentrations of dissolved iron, mercury, zinc, and copper remained about the same at the upper and lower extremes of the stream. In contrast, the levels of suspended iron, arsenic, and manganese show significant increases at the lower site. Selenium shows the opposite trend; levels were higher at the upper extreme and decreased significantly at the lower end of the stream. The increases in iron, arsenic, and manganese can be explained by the large quantities of these elements in the groundwater aquifers; these contribute more water to the stream at lower elevations. However, the level of selenium was also higher in the groundwater aquifers, but decreased at downstream sites. The different behavior pattern for selenium is emphasized by its spatial and temporal distribution curve (Figure 18) compared with those of either arsenic (Figure 19), which, along with selenium, was always detectable, or the common ions (Figures 11-16), which all follow a common pattern. In this pattern, the highest levels were observed farthest downstream during the June-August season. The level of selenium was usually lower at P7 than at any upstream sites and was particularly low during the June-August season. This suggests that selenium may be removed from the stream by some chemical or biological process that is inoperative for any of the other trace elements analyzed. Alternatively, its removal from solution by reaction with the increased levels of suspended iron found at P7 may be responsible. Howard (1972) has shown that the geochemical behavior of selenium in natural waters is controlled by adsorption on hydrous ferric oxides. The equilibrium conditions characteristic of such a removal process are present in Piceance Creek.

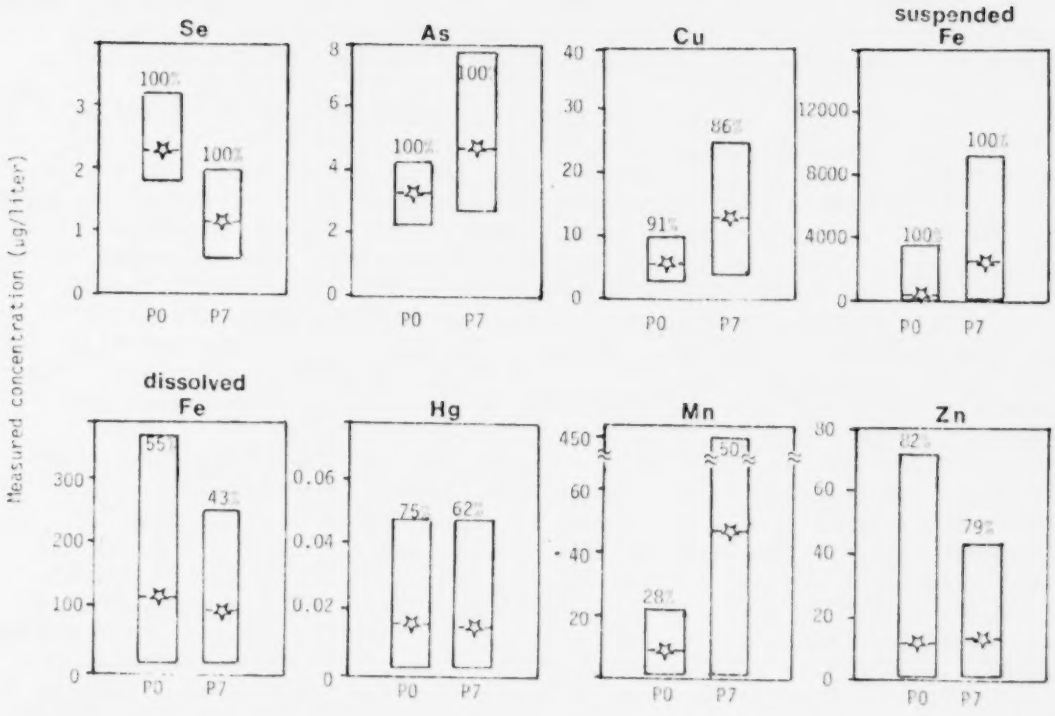


Figure 17. Range of measured concentrations, frequency of occurrence above detection limits, and average concentrations above (P0) and below (P7) Tract C-b. (When frequency of occurrence above detection is less than 100%, the lower limit of bar indicates detection limit; the upper limit of all bars indicates maximum observed concentration; ☆ indicates average concentration observed. Percentage value indicates frequency with which the concentration was above the detection limit.)

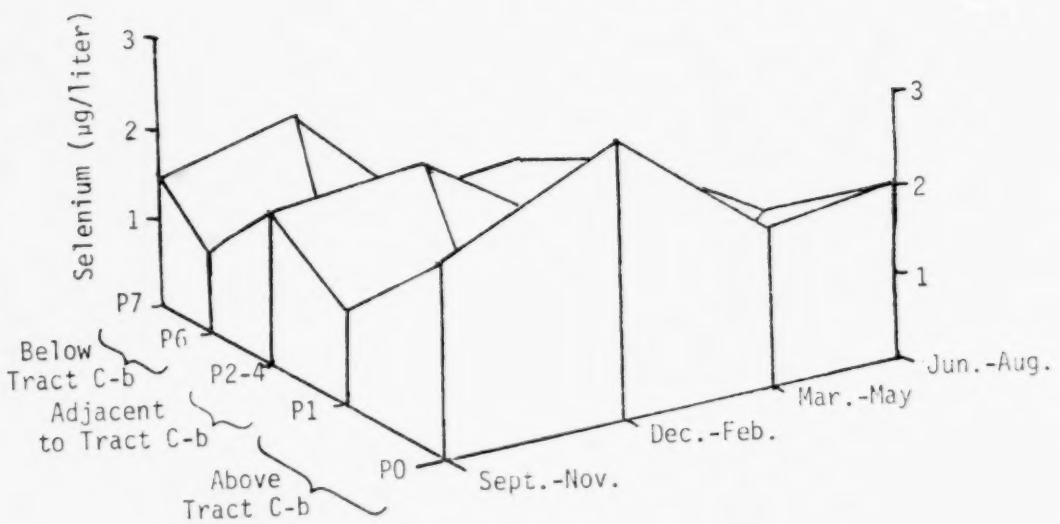


Figure 18. Spatial and temporal distribution of selenium concentration.

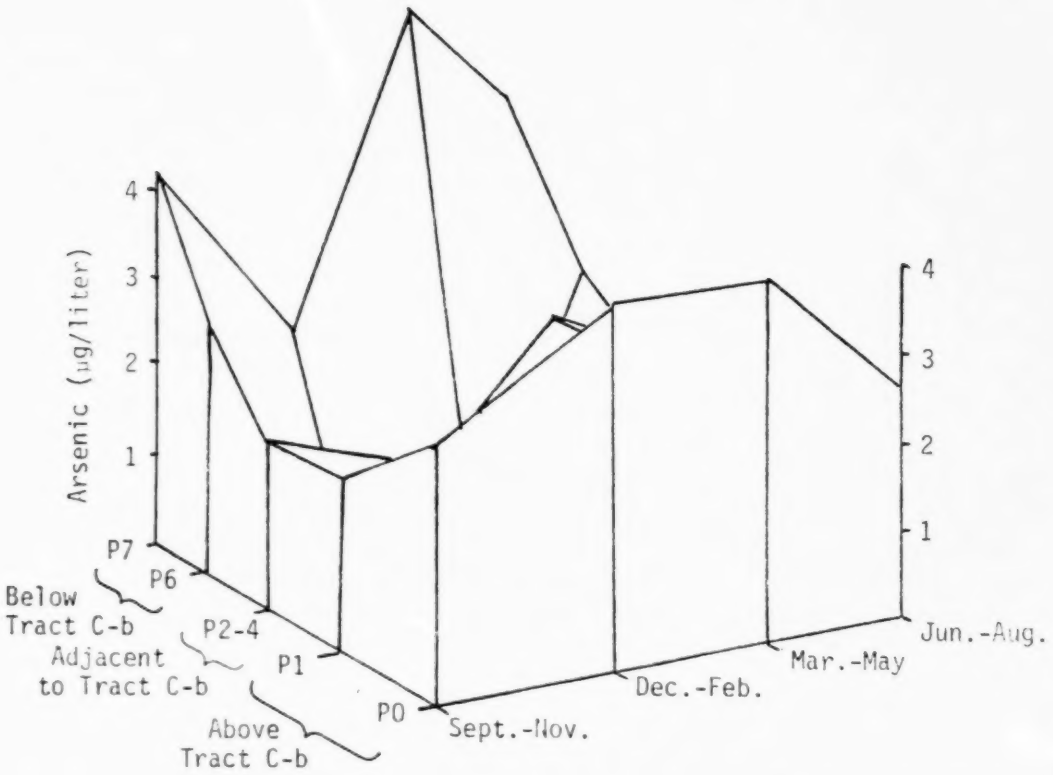


Figure 19. Spatial and temporal distribution of arsenic concentration.

## SECTION VIII

## EVALUATION OF CHEMICAL EQUILIBRIA

The low levels of the heavy metals are consistent with the expectation that chemical factors play roles in controlling the soluble metal ion concentrations. The high levels of sulfate and alkalinity, coupled with the relative constancy of pH, makes it quite likely that complexation and precipitation equilibria involving sulfate, carbonate, and hydroxide may limit the levels of several trace elements to low levels. The limiting concentrations of several trace metals have therefore been calculated using the methods described previously (Skogerboe et al., 1979). This description has been included as Appendix A. In brief, the average levels of alkalinity (bicarbonate), sulfate, chloride, and pH are taken as representative limiting boundary conditions; the controlling precipitates are determined via solubility calculations; and the possible increases in solubility due to complexation are estimated by calculation. This results in an estimate of the upper limit value for total dissolved metal. Equilibrium calculations have not been carried out for the non-metals, arsenic and selenium, because the levels of these elements are believed to be controlled by other factors (Hem, 1970; Howard, 1972).

Plots of the calculated maximum levels of dissolved metal versus pH have been prepared for the average conditions observed at sites PO and P7 on Piceance Creek. Streams such as this are exposed to oxygen from the atmosphere and are thus expected to exhibit oxidizing conditions. However, in natural water systems, kinetic factors rather than oxygen availability may be important in determining oxidation state and, since different redox mechanisms may be operative for different elements, some metals may exist in an oxidized form while others remain largely in a reduced form (Hem, 1970). Therefore, for metals having more than one common oxidation state, each state was considered separately.

The resulting data (Figures 20-22) show that the solubilities of most metal ions are at minimum levels near the pH characteristic of Piceance Creek. At lower pH values, protonation of anions (e.g., $OH^-$ to $H_2O$, $CO_3^{2-}$ to $HCO_3^-$ and $H_2CO_3$) decreases the importance of precipitation and increases the metal ion solubilities. At high pH values, the formation of soluble hydroxide complexes usually increases metal ion solubilities. Hence the naturally occurring pH along Piceance Creek (7.5-8.5) is at or near the optimum level for maintaining low levels of metals in solution. In Table 5 the observed maximum concentrations are compared with those calculated for the average conditions observed at sites PO and P7. For mercury, zinc, copper, manganese, and lead the actual observed levels were far below those calculated for the 2+ oxidation states of the metals (the most likely oxidation state present).

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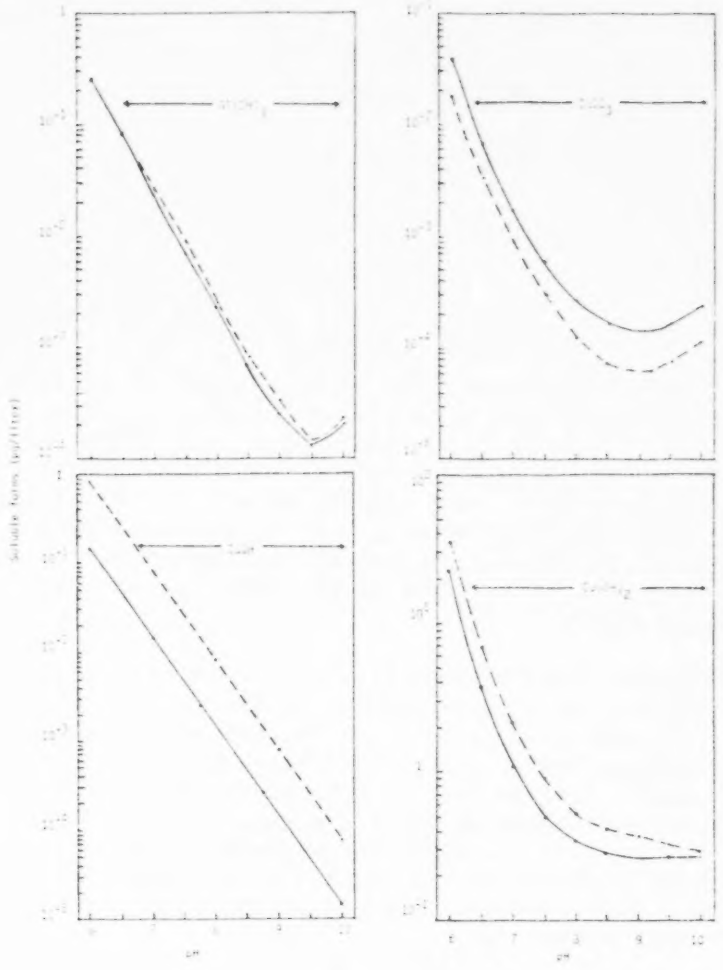

Figure 20. Solubilities of Al, Cd, and Cu under conditions typical of Piceance Creek. —— Conditions representative of upper Piceance Creek [$HCO_3$] = 360, [$SO_4$] = 125, [Cl] = 1, [$PO_4$] = 0.01 (in mg/liter). --- Conditions representative of lower Piceance Creek [$HCO_3$] = 1080, [$SO_4$] = 450, [Cl] = 42, [$PO_4$] = 0.01 (in mg/liter). The precipitating forms of the elements, which control the solubility over the indicated ranges, are given on the figures.

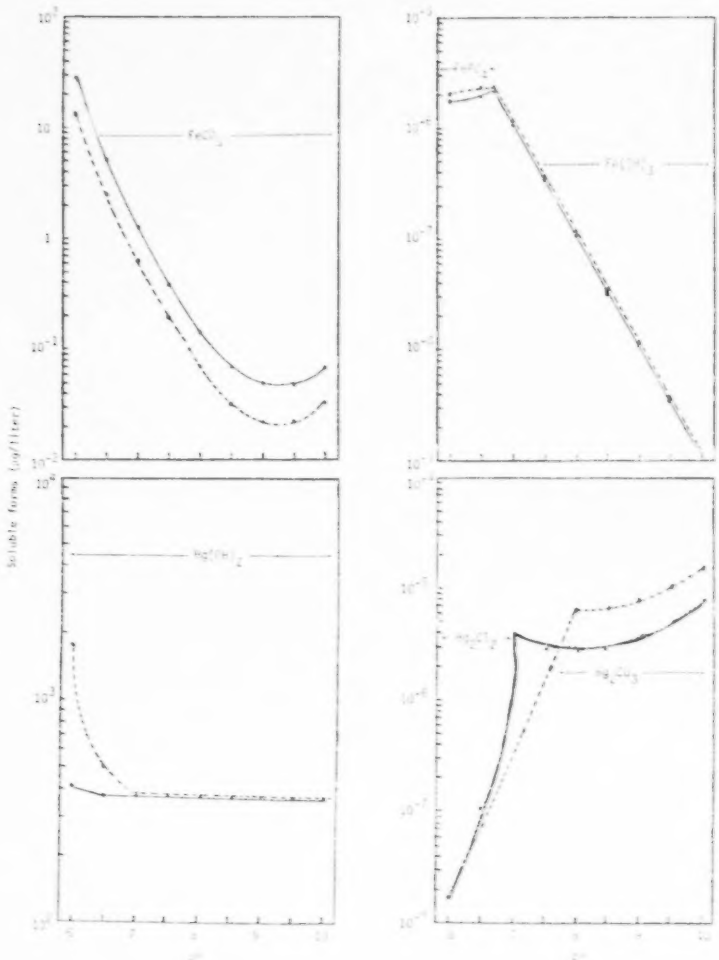

Figure 21. Solubilities of Fe and Hg under conditions typical of Piceance Creek. —— Conditions representative of upper Piceance Creek $[HCO_3]$ = 360, $[SO_4]$ = 125, [Cl] = 1, $[PO_4]$ = 0.01 (in mg/liter). --- Conditions representative of lower Piceance Creek $[HCO_3]$ = 1080, $[SO_4]$ = 450, [Cl] = 42, $[PO_4]$ = 0.01 (in mg/liter). The precipitating forms of the elements, which control the solubility over the indicated ranges, are given on the figures.

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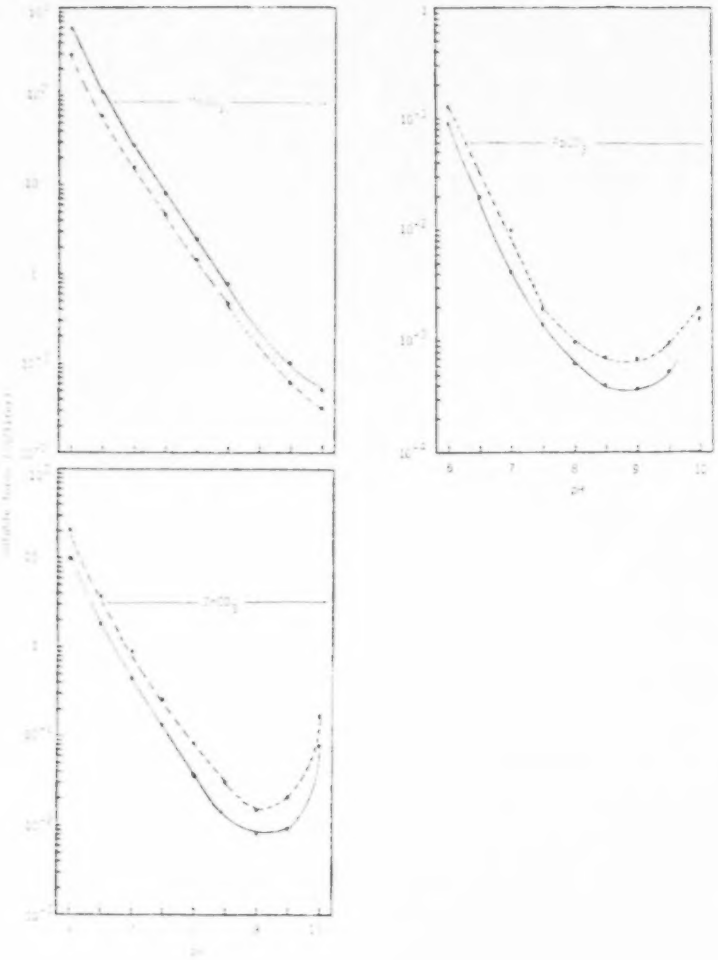

Figure 22. Solubilities of Mn, Pb, and Zn under conditions typical of Piceance Creek. —— Conditions representative of upper Piceance Creek [$HCO_3$] = 360, [$SO_4$] = 125, [Cl] = 1, [$PO_4$] = 0.01 (in mg/liter). --- Conditions representative of lower Piceance Creek [$HCO_3$] = 1080, [$SO_4$] = 450, [Cl] = 42, [$PO_4$] = 0.01 (in mg/liter). The precipitating forms of the elements, which control the solubility over the indicated ranges, are given on the figures.

TABLE 5. CALCULATED AND OBSERVED MAXIMUM CONCENTRATIONS (µG/LITER) ALONG PICEANCE CREEK COMPARED WITH USPHS LIMITS AND U.S. EPA CRITERIA FOR FRESHWATER AQUATIC LIFE

| Metal | P0[a] | | P7[b] | | Drinking water (USPHS, 1962) | Aquatic life (U.S. Environmental Protection Agency, 1977) |
|---|---|---|---|---|---|---|
| | Calculated maximum[c] | Observed maximum[d] | Calculated maximum[e] | Observed maximum[d] | | |
| Cd(II) | 0.3 | <5.0 | 0.1 | <5.0 | 10 | 0.4-12.0 |
| Hg(I) | 1.6 | 0.5 | 0.6 | 0.14 | --[f] | 0.05 |
| Hg(II) | 360,000 | | 360,000 | | -- | |
| Al(III) | 2.4 | <100.0 | 1.6 | <100.0 | -- | -- |
| Zn(II) | 85.0 | 0.72 | 28.0 | 0.044 | 5000 | 0.01 × 96-h $LC_{50}$ |
| Cu(I) | 1.5 | 10.0 | 5.2 | 25.0 | 1000 | 0.1 × 96-h $LC_{50}$ |
| Cu(II) | 350.0 | | 480.0 | | 1000 | |
| Fe(II) | 140.0 | 190.0 | 50.0 | 130.0 | 300 | 1000 |
| Fe(III) | 0.0001 | | 0.0001 | | 300 | |
| Mn(II) | 2500.0 | 22.0 | 930.0 | 450.0 | 50 | -- |
| Pb(II) | 1.0 | <0.2 | 0.5 | 0.02 | 50 | 0.01 × 96-h $LC_{50}$ |

[a] Upper limit of creek.

[b] Lower limit of creek.

[c] Conditions: pH = 8.0; alk = 300 mg $CaCO_3$/liter; $[SO_4]$ = 125 mg/liter; [Cl] = 1 mg/liter; $[PO_4]$ = 0.01 mg/liter.

[d] For metals with more than one common oxidation state, the observed level is for total dissolved metal and does not distinguish between oxidation states.

[e] Conditions: pH = 8.2; alk = 1080 mg $CaCO_3$/liter; $[SO_4]$ = 450 mg/liter; [Cl] = 42 mg/liter; $[PO_4]$ = 0.01 mg/liter.

[f] Dashed lines indicate no limit given.

This suggests that if future influxes of these metals occur, their levels may increase beyond their present levels but they are less likely to exceed the calculated levels unless unknown complexing agents are also present. The concentration of iron is already above the level calculated assuming either Fe(II) or Fe(III). This suggests that factors other than precipitation and complexation may be operative. One explanation is that iron(III) hydroxide may be present in a very finely divided particulate form that passes through 0.45 micron filters, thus being measured as soluble iron. Another explanation for the high observed iron levels is that complexation by organic species may increase its solubility beyond that expected via purely inorganic control.

For comparative purposes, a summary of the USPHS limits for safe drinking water is also given in Table 5, and Table 6 shows EPA limits for aquatic life and domestic water supplies (U.S. Environmental Protection Agency, 1977). These are far above the calculated and observed levels for all metals except manganese. Thus, although increases in the concentrations of metal ions may still occur, they may be limited to levels that are still safe.

As indicated by the solubility curves for the metals (Figures 20-22), metal ion solubilities are generally expected to be low under the conditions characteristic of the downstream portion of Piceance Creek. For copper, however, the solubility is expected to increase under downstream conditions. The explanation for this is found in Table 7 which lists the major chemical forms of the soluble metal. The values given in parentheses after each metal complex are the percentages of the total metal present in this form in the pH range 7.5-8.5. For copper(I), or copper(II), the major soluble forms are $CuCl^0$ or $CuOH_2{}^0$, respectively, while the controlling precipitate is the hydroxide. Thus the *free* copper concentration depends only on pH and is the same for both sets of conditions, but the *total* copper solubility is increased when more $Cl^-$ [for Cu(I)] or $OH^-$ [for Cu(II)] is present; downstream conditions are characterized by larger concentrations of both of these ions.

Another salient feature apparent in Table 7 is the large role played by pH in determining chemical forms. Most frequently, the metal ions exist largely as either the aquated species or as a hydroxo species; the pH determines the ratio. Thus, small shifts in pH should significantly alter the major form of these metal ions in solution. The highly alkaline nature of stream conditions along Piceance Creek will serve to maintain the current pH levels in the event of small perturbations. However, a major influx of acidic or caustic material that exceeds the buffer capacity would greatly alter not only the total solubility, but also the form of the soluble metal ion.

TABLE 6. SELECTED WATER QUALITY CRITERIA
(U.S. ENVIRONMENTAL PROTECTION AGENCY, 1977)

| Parameter | Freshwater aquatic life | Drinking water |
|---|---|---|
| Alkalinity | ≥ 20 mg/liter | -- |
| Arsenic | -- | 50 µg/liter |
| Cadmium | 0.4-4 µg/liter (soft water)[a/]<br>1.2-12 µg/liter (hard water) | 10 µg/liter |
| Chromium | 100 µg/liter | 50 µg/liter |
| Copper | 0.1 × a 96-h $LC_{50}$[b/] | 1.0 mg/liter |
| Iron | 1.0 mg/liter | 0.3 mg/liter |
| Lead | 0.01 × a 96-h $LC_{50}$ | 50 µg/liter |
| Manganese | -- | 50 µg/liter |
| Mercury | 0.05 µg/liter | 2.0 µg/liter |
| Nickel | 0.01 × a 96-h $LC_{50}$ | -- |
| Dissolved oxygen | 5.0 mg/liter minimum | -- |
| pH | 6.5 to 9.0 | 5.0 to 9.0 |
| Selenium | 0.01 × a 96-h $LC_{50}$ | 10 µg/liter |
| Silver | 0.01 × a 96-h $LC_{50}$ | 50 µg/liter |

[a/] Soft water: 0-75 mg/liter $CaCO_3$; hard water: 150-300 mg/liter $CaCO_3$

[b/] $LC_{50}$ is defined as the concentration of a toxicant which is lethal to 50% of the organisms tested under the test conditions in a specified time. (The receiving or comparable water should be used as the diluent for sensitive freshwater resident species.)

TABLE 7. SUMMARY OF RESULTS OF EQUILIBRIUM CALCULATIONS: CONTROLLING PRECIPITATE AND PRIMARY CHEMICAL FORMS OF SOLUBLE METALS

| Metal ion | Controlling precipitate | Soluble forms | |
|---|---|---|---|
| | | Upstream conditions[a] | Downstream conditions[b] |
| $Al^{3+}$ | $Al(OH)_3$ | $Al(OH)_2^+$ (100)[c] | $Al(OH)_2^+$ (100) |
| $Cd^{2+}$ | $CdCO_3$ | $Cd^{2+}_{(aq)}$(78-27) | $Cd(aq)^{2+}$(78-27) |
| | | $CdOH^+$(21-72) | $CdOH^+$(21-72) |
| $Cu^+$ | CuOH | $Cu^+_{(aq)}$(10) | $Cu^+_{(aq)}$(2) |
| | | $CuCl^0$(90) | $CuCl^0$(97) |
| | | | $CuCl_2^-$ (1) |
| $Cu^{2+}$ | $Cu(OH)_2$ | $Cu(OH)_2^0$(52-89) | $Cu(OH)_2^0$(29-63) |
| | | $CuCO_3^0$(37-6) | $CuCO_3^0$(56-12) |
| | | $Cu(CO_3)_2^{2-}$(2-3) | $Cu(CO_3)_2^{2-}$(10-24) |
| | | $Cu^{2+}_{(aq)}$(4-0.01) | $Cu^{2+}_{(aq)}$(3-0) |
| | | $CuSO_4^0$(0.3-0) | $CuSO_4^0$(0.4-0) |
| $Fe^{2+}$ | $FeCO_3$ | $Fe^{2+}_{(aq)}$(84-46) | $Fe^{2+}_{(aq)}$(82-50) |
| | | $FeOH^+$(9-51) | $FeOH^+$(7-44) |
| | | $FeSO_4^0$(6-3) | $FeSO_4^0$(10-6) |
| $Fe^{3+}$ | $Fe(OH)_3$ | $Fe(OH)_3^0$(100) | $Fe(OH)_3^0$(100) |
| $Pb^{2+}$ | $PbCO_3$ | $Pb^{2+}_{(aq)}$(56-15) | $Pb^{2+}_{(aq)}$(67-23) |
| | | $PbOH^+$(30-78) | $PbOH^+$(20-69) |
| | | $PbSO_4^0$(13-3) | $PbSO_4^0$(12-4) |
| | | $Pb(OH)_2^0$(0.1-3) | $Pb(OH)_2^0$(0-2) |
| | | | $PbCl^+$(1.5-0.5) |

TABLE 7. Continued.

| Metal ion | Controlling precipitate | Soluble forms: Upstream conditions[a] | Soluble forms: Downstream conditions[b] |
|---|---|---|---|
| $Mn^{2+}$ | $MnCO_3$ | $Mn^{2+}_{(aq)}$(80) | $Mn^{2+}_{(aq)}$(67) |
| | | $MnHCO_3^-$(15) | $MnHCO_3^-$(25) |
| | | $MnSO_4^0$(5) | $MnSO_4^0$(7) |
| $Hg_2^{2+}$ | $Hg_2CO_3$ | $Hg_2OH^+$(98-100) | $Hg_2OH^+$(98-100) |
| | | $Hg_2SO_4^0$(1) | $Hg_2SO_4^0$(1) |
| $Hg^{2+}$ | $Hg(OH)_2$ | $Hg(OH)_2^0$(100) | $Hg(OH)_2^0$(100) |
| $Zn^{2+}$ | $ZnCO_3$ | $Zn^{2+}_{(aq)}$(92-76) | $Zn^{2+}_{(aq)}$(88-76) |
| | | $ZnOH^+$(2-19) | $ZnOH^+$(1-15) |
| | | $ZnSO_4^0$(6-5) | $ZnSO_4^0$(10-18) |

[a] Upstream conditions: alk = 300 mg $CaCO_3$/liter, $[SO_4]$ = 125 mg/liter, [Cl] = 7 mg/liter, $[PO_4]$ = 0.01 mg/liter.

[b] Downstream conditions: alk = 850 mg $CaCO_3$/liter, $[SO_4]$ = 450 mg/liter, [Cl] = 42 mg/liter, $[PO_4]$ = 0.01 mg/liter.

[c] The values in parentheses are the predicted percentages present in these forms in the pH range 7.5-8.5.

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# APPENDIX A

# EVALUATION OF HEAVY METAL EQUILIBRIA*

*This Appendix was taken largely from Skogerboe, R. K., C. S. Lavallee, M. M. Miller, and D. L. Dick. 1979. Environmental Effects of Western Coal Surface Mining. Part III - The Water Quality of Trout Creek, Colorado, Ecol. Res. Ser., U.S. Environmental Protection Agency, Duluth, Minn. (In press)

Fairly comprehensive water quality data sets have been accumulated by us[1,2] and by state water resource agencies, USGS, and EPA for western streams. Examination of these data indicates that the general water quality characteristics are quite similar on a broad scale. Based on this examination the following generalizations can be made.

1. Observed pH values range from 6.5 to 8.5 with more than 85% of all values falling between 7 and 8.

2. Total alkalinity ranges from 20-1000 mg carbonate/liter with the most common values approximating 100 mg/liter. Acidity is typically immeasurable and rarely approaches 10 mg/liter.

3. Total hardness ranges up to 2500 mg $CaCO_3$/liter with most values lying in the 150-200 mg/liter range.

4. Total sulfate covers the 10-2500 mg/liter range with values around 150-200 mg/liter being most frequent.

5. Chloride concentrations rarely exceed 1 mg/liter.

6. Nitrate concentrations rarely exceed 1 mg/liter.

7. Orthophosphate levels are typically less than 0.1 mg/liter.

These parameters may be generally considered primary in controlling the chemical equilibria which determine the solubilities of many heavy metals.

In view of the mineralogical and/or chemical characteristics of the soils, sediments, and mine overburden/spoils of this region, the general concentration levels of the anionic species cited above should be essentially "fixed" in the ranges mentioned above. Moreover, the morphologies of most western streams are such that their waters will remain in reasonable equilibrium with atmospheric constituents such as $CO_2$ and $O_2$ as influenced by other parameters such as pH, temperature, alkalinity, etc. Simply stated, the observed ranges of pH, carbonate, alkalinity, sulfate, etc., can be defined as generally representative of the entire western coal development region.

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[1]Skogerboe, R. K., C. S. Lavallee, M. M. Miller, and D. L. Dick. 1978. Effects of a surface coal mine on water quality: Trout Creek, Colorado. Compilation of chemical data. NREL-FBL Tech. Rep. No. 1. Natural Resource Ecology Laboratory, Colorado State Univ., Fort Collins, CO, and Fisheries Bioassay Laboratory, Montana State Univ., Bozeman, MT. 173 p.

[2]Skogerboe, R. K., C. S. Lavallee, M. M. Miller, and D. L. Dick. 1978. Preoperational surface water quality conditions along Piceance Creek, Colorado: Compilation of chemical data. NREL-FBL Tech. Rep. No. 2. Natural Resource Ecology Laboratory, Colorado State Univ., Fort Collins, CO, and Fisheries Bioassay Laboratory, Montana State Univ., Bozeman, MT. 73 p.

These ranges can consequently be taken as boundary conditions in considering the heavy metal equilibria that should prevail in the *absence* of unusual circumstances. The ranges given above should, within limits, be relatively unperturbed by the additions of other constituents such as metal ions unless such additions involve *major* influxes. Consequently, equilibrium models can be used for predicting the fates of heavy metals which may be available in forms soluble under other conditions.

Equilibrium calculations can thus be used to estimate *maximum solubilities* of several heavy metals under the conditions representative of the chemical and mineralogical features of the soils and spoils and the ground and surface waters of the area. These calculations may be made assuming that the heavy metals in question exist in soluble forms at their origin, e.g., a strip coal mine. If they do not, the maximum solubility calculations will be overestimates of the actual case. It can be easily argued that such definitions of upper limits serve as valuable reference points.

Two general types of chemical interactions may occur for a particular metal ion and any combination of the anionic species stipulated in the above set of generalizations. Immobilization of the metal ion due to precipitation or to ion exchange type processes may occur. Alternatively, the ion may be mobilized by complexation reactions which effectively enhance its solubility. In either case, the interactions involved can be described by thermodynamic parameters. The relative significance levels of the possible equilibria can therefore be assessed on the basis of thermodynamic stabilities. Reactions resulting in the largest increases in stability will tend to be principal among the various possibilities. The compilation of equilibrium constants published by Sillen and Martell[3] has been used as the data source for the present calculations.

The equilibria considered for each metal ion are listed in Appendix Table 1. Precipitates of a complex nature [e.g., $Zn(CO_3)_{0.36}(OH)_{1.28}$] were not considered since such precipitates are usually formed only slowly from simpler precipitates (e.g., $ZnCO_3$) rather than directly in solution. They will, therefore, not be the controlling equilibria on the time scale of importance herein, i.e., a few days. Some other equilibria could also have been included, but were rejected either because: (i) their equilibrium constants were too low to be considered significant relative to those listed, or (ii) the concentrations of the anions involved indicated a lack of significance. The equilibria in Appendix Table 1 have been written so the stoichiometric coefficient of the aquated metal ion is unity. This practice has been followed to simplify model calculations. The equilibrium constants used in the calculations are also given in Appendix Table 1; values chosen were for 25°C and zero ionic strength. In instances for which two or more independent determinations of an equilibrium constant did not agree, average values were selected for the present calculations. For metals having more

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[3]Sillen, L. G., and A. F. Martell. 1964. Stability constants of metal-ion complexes. Spec. Publ. No. 17. Chemical Society, London.

than one common oxidation state, all states were considered because the redox characteristics of the waters may vary significantly. In all calculations, the pH was selected as the independent (master) variable. The common ranges for each of the anions present, as indicated above, were used to define the boundary conditions for the calculations. Thus, the low and high ends of the typical concentration range for each anion were used in the calculations as a means of defining the extremes of the controlling equilibria possibilities. For anions that could be present in various forms, the pH-based calculations were used to determine the relative concentrations of each form. Carbonate, for example, may be present as dissolved $CO_2$, $H_2CO_3$, $HCO_3^-$, $CO_3^{2-}$, $CaHCO_3^+$, and $CaCO_3^0$. The species $CaHCO_3^+$ and $CaCO_3^0$ are soluble complexes which, because of the typically high levels of calcium in solution (>60 mg/liter) may tie up a significant fraction of the total carbonate. The appropriate equilibrium constants were consequently used to determine the respective concentrations of each of the free carbonate species at the pH level in question. The carbonate boundary condition concentrations, given as a footnote to Table 5, are thus for the total of all carbonate related species. Similar adjustments were made for other anions as required.

Since the interest is in obtaining estimates of the maximum concentration of soluble metal, any effect which will tend to increase solubility should be taken into account. The effect of ionic strength is such that solubilities of metal salts will be increased at higher ionic strength; hence a correction for ionic strength has been made; i.e., the equilibrium calculations are carried out in terms of activities which are related to concentrations by the relation:

$$a = \gamma C.$$

The activity coefficient $\gamma$ decreases with increasing ionic strength, where ionic strength, I, is defined by

$$I = \tfrac{1}{2} \sum_i C_i z_i^2,$$

where $z_i$ is the charge of the ith ionic species and $C_i$ is its molar concentration. The activity coefficients have been calculated for the typical concentration ranges cited above via the equation:

$$\log \gamma_{\pm z} = -A\, z^2 \frac{\sqrt{I}}{1 + \sqrt{I}} \qquad (1)$$

where A is a constant whose value depends only on the solvent and temperature. This equation is generally accepted as the best available for estimating the value of $\gamma$ in an aqueous system containing more than one salt (i.e., a mixed electrolyte system)[4]. Failure to include an ionic strength correction lowers

[4]Stumm, W., and J. J. Morgan. 1970. Aquatic chemistry. Wiley-Interscience, New York.

the calculated total metal solubilities by 5-10% for typical stream conditions and by 530% for typical mine spoil drainage conditions.

As indicated above, reactions between metal ions and anions may involve precipitation or complexation. The general expression for precipitation of a metal ion, $M^{n+}$, by an anion, $A^{m-}$, is:

$$M^{n+} + n/m\ A^{m-} \rightleftharpoons 1/m\ M_mA_n \tag{2}$$

and

$$K_{sp} = (M^{n+})(A^{m-})^{n/m} \tag{3}$$

where parentheses indicate the *activities* of the species. A similar expression for complexation would be:

$$M^{n+} + qA^{m-} \rightleftharpoons MA_1^{+n-(qm)} \tag{4}$$

and

$$K_1 = \frac{(MA_q^{n-qm})}{(M^{+n})(A^{-m})^q} \tag{5}$$

Considering the equilibria for $Zn^{2+}$ as an example (Appendix Table 1) the following expressions may be evaluated.

$$(Zn^{2+}) = 10^{15.7}/(OH^-)^2 \tag{6}$$

$$(Zn^{2+}) = 10^{-10.8}/(CO_3^{2-}) \tag{7}$$

$$(Zn^{2+}) = 10^{-14.42}/(CO_3^{2-})^{0.36}(OH^-)^{1.28} \tag{8}$$

$$(Zn^{2+}) = 10^{-10.68}/(PO_4^{3-})^{2/3} \tag{9}$$

and

$$(Zn^{2+}) = 10^{-13.9}/(SO_4^{2-})^{1/4}(OH^-)^{3/2} \tag{10}$$

Thus, for example, at pH = 7; $(OH^-) = 10^{-7}$ M; $(PO_4^{3-}) = 10^{-5}$ M; and total carbonate species $(CO_3)_T = 3 \times 10^{-3}$ M; it may be determined that the solubility of Zn will be limited principally by carbonate precipitation (Equation 7) to a molarity of $10^{-5}$. This calculation has consequently defined the controlling precipitate as well as the upper limit concentration of $Zn^{2+}$. The quantity of interest is the total soluble zinc which is the experimentally determined quantity regardless of chemical form. Again referring to Appendix Table 1, the total soluble Zn, $(Zn)_T$, may be defined as the sum of all dissolved Zn-containing species, i.e.,

$$(Zn)_T = (Zn^{2+})/\gamma\pm 2 + (ZnOH^+)/\gamma\pm 1 + (Zn(OH)_3^-)/\gamma\pm 1$$
$$+ (Zn(OH)_4^{2-})/\gamma\pm 2 + (ZnSO_4^0) + (ZnCl^+)/\gamma\pm 1 + \quad (11)$$
$$(ZnCl_2^0) + (ZnCl_3^-)/\gamma\pm 1 + (ZnCl_4^{2-})/\gamma\pm 2$$

The concentrations of each of these complexes may be expressed in terms of the $Zn^{2+}$, the appropriate anion concentration, and the respective equilibrium constants. Equation 11 may be reduced to:

$$(Zn)_T = (Zn^{2+}) \{1/\gamma\pm 2 + 10^{5.04}(OH^-)/\gamma\pm 1$$
$$+ 10^{14.2} (OH^-)^3/\gamma\pm 1 + 10^{15} (OH^-)^4/\gamma\pm 1 \quad (12)$$
$$+ 10^{2.26} (SO_4^{2-}) + 10^{0.43} (Cl^-)/\gamma\pm 1$$
$$+ \ldots 10^{0.2} (Cl^-)^4/\gamma\pm 2\}$$

Evaluation of this for the pH = 7 conditions listed above when $(Zn^{2+}) = 10^{-5}$ indicates that the total soluble Zn concentration when complexation reactions are considered may be increased to $2.4 \times 10^{-5}$ M. This coincides with a concentration of ~1.6 mg/liter. These same calculation procedures are carried out for a given set of boundary conditions for the metals listed in relation to pH.

APPENDIX TABLE 1. EQUILIBRIA AND EQUILIBRIUM CONSTANTS CONSIDERED IN MODEL CALCULATIONS[a/]

| Species | Product(s) | log K |
|---|---|---|
| $H_2O$ | $H^+ + OH^-$ | -14 |
| $H_2CO_3$ | $H^+ + HCO_3^-$ | -6.35 |
| | $H^+ + CO_3^{2-}$ | -10.34 |
| | $CaHCO_3^+$ | 1.26 |
| | $CaCO_3^0$ [b/] | 3.2 |
| $H_2SO_4$ | $H^+ + SO_4^{2-}$ | -1.99 |
| | $CaSO_4^0$ | 2.31 |
| $H_3PO_4$ | $H^+ + H_2PO_4^-$ | -2.16 |
| | $H^+ + HPO_4^{2-}$ | -7.21 |
| | $H^+ + PO_4^{3-}$ | -12.33 |
| Al(III) | $Al(OH)_3$ | -32.5 |
| | $AlPO_4$ | -18.24 |
| | $AlOH^{2+}$ | 9.76 |
| | $Al(OH)_2^+$ | 19.4 |
| | $Al(OH)_4^-$ | 28.3 |
| | $AlSO_4^+$ | 3.2 |
| | $Al(SO_4)_2^-$ | 5.1 |
| Cd(II) | $CdCO_3$ | -13.74 |
| | $Cd(OH)_{1.5}(SO_4)_{0.25}$ | -12.5 |
| | $1/3\ Cd_3(PO_4)_2$ | -10.72 |
| | $CdSO_4$ | -7.8 |
| | $Cd(OH)_2$ | -14.5 |
| | $CdOH^+$ | 6.08 |

Appendix Table 1. Continued.

| Species | Product(s) | log K |
|---|---|---|
| Cd(II) (cont.) | $Cd(OH)_2^0$ | 8.7 |
| | $Cd(OH)^-$ | 8.38 |
| | $Cd(OH)_4^{2-}$ | 8.42 |
| | $CdSO_4^0$ | 2.3 |
| | $CdCl^+$ | 1.95 |
| | $CdCl_2^0$ | 2.5 |
| | $CdCl_3^-$ | 2.35 |
| | $CdCl_4^{2-}$ | 1.65 |
| Cu(II) | $Cu(OH)_2$ | -19.7 |
| | $CuCO_3$ | -9.63 |
| | $1/3\ Cu_3(PO_4)_2$ | -12.3 |
| | $CuOH^+$ | 6.66 |
| | $Cu(OH)_2^0$ | 14.32 |
| | $Cu(OH)_3^-$ | 15.5 |
| | $Cu(OH)_4^{2-}$ | 13.8 |
| | $1/2\ Cu_2(OH)_2^{2+}$ | 5.26 |
| | $CuCO_3^0$ | 6.34 |
| | $Cu(CO_3)_2^{2-}$ | 10.01 |
| | $CuCO_3OH^-$ | 15.0 |
| | $CuSO_4^0$ | 2.35 |
| | $CuCl^+$ | 0.95 |
| $Hg_2$(II) | $Hg_2CO_3$ | -16.05 |
| | $Hg_2HPO_4$ | -12.4 |

Appendix Table 1. Continued.

| Species | Product(s) | log K |
|---|---|---|
| $Hg_2$(II) (cont.) | $Hg_2Cl_2$ | -17.88 |
| | $Hg_2OH^+$ | 9.0 |
| | $Hg_2SO_4{}^0$ | 1.3 |
| | $Hg_2(SO_4)_2{}^{2-}$ | 2.4 |
| Hg(II) | $Hg(OH)_2$ | -25.4 |
| | $HgOH^+$ | 10.2 |
| | $Hg(OH)_2{}^0$ | 22.66 |
| | $Hg(OH)_3{}^-$ | 21.8 |
| | $Hg(OH)_4{}^{2-}$ | 21.3 |
| | $HgSO_4{}^0$ | 1.34 |
| | $Hg(SO_4)_2{}^{2-}$ | 2.44 |
| | $HgCl^+$ | 6.74 |
| | $HgCl_2{}^0$ | 13.22 |
| | $HgCl_3{}^-$ | 13.79 |
| | $HgCl_4{}^{2-}$ | 15.25 |
| Mn(II) | $Mn(OH)_2$ | -12.8 |
| | $MnCO_3$ | -9.3 |
| | $MnOH^+$ | 3.41 |
| | $Mn(OH)_3{}^-$ | 1.8 |
| | $MnHCO_3{}^+$ | 1.8 |
| | $MnSO_4{}^0$ | 2.26 |
| Pb(II) | $Pb(OH)_2$ | -18.7 |
| | $PbCO_3$ | -13.4 |

Appendix Table 1. Continued.

| Species | Product(s) | log K |
|---|---|---|
| Pb(II) (cont.) | 1/3 $Pb_3(PO_4)_2$ | -14.03 |
| | $PbHPO_4$ | -9.9 |
| | $PbCl_2$ | -4.76 |
| | $PbSO_4$ | -7.8 |
| | $PbOH^+$ | 6.22 |
| | $Pb(OH)_2^0$ | 10.34 |
| | $Pb(OH)_3^-$ | 13.95 |
| | $Pb_2OH^{3+}$ | 6.7 |
| | $Pb_4(OH)_4^{4+}$ | 35.7 |
| | $PbCl^+$ | 1.6 |
| | $PbCl_2^0$ | 1.78 |
| | $PbCl_3^-$ | 1.68 |
| | $PbCl_4^{2-}$ | 1.38 |
| | $PbSO_4^0$ | 2.46 |
| Zn(II) | $Zn(OH)_2$ | -15.7 |
| | $ZnCO_3$ | -10.8 |
| | 1/3 $Zn_3(PO_4)_2$ | -10.68 |
| | $ZnOH^+$ | 5.04 |
| | $Zn(OH)_3^-$ | 14.2 |
| | $Zn(OH)_4^{2-}$ | 15.0 |
| | $ZnSO_4^0$ | 2.26 |
| | $ZnCl^+$ | 0.43 |

Appendix Table 1. Continued.

| Species | Product(s) | log K |
|---|---|---|
| Zn(II) (cont.) | $ZnCl_2^0$ | 0.61 |
| | $ZnCl_3^-$ | 0.53 |
| | $ZnCl_4^{2-}$ | 0.2 |
| Fe(II) | $Fe(OH)_2$ | -15.1 |
| | $FeCO_3$ | -10.6 |
| | $FeOH^+$ | 5.7 |
| | $Fe(OH)_3^-$ | 10.0 |
| | $Fe(OH)_4^{2-}$ | 9.6 |
| Fe(III) | $Fe(OH)_3$ | -38.6 |
| | $FePO_4$ | -30.02 |
| | $Fe(OH)H_2PO_4$ | -34.56 |
| | $FeOH^{2+}$ | 11.81 |
| | $Fe(OH)_2^+$ | 20.84 |
| | $Fe(OH)_4^{2-}$ | 24.54 |
| | $FeSO_4^+$ | 4.10 |
| | $FeCl^{2+}$ | 1.48 |
| | $Fe(SO_4)_2^-$ | 5.44 |

a/ Sillen, L. G., and A. F. Martell. 1964. Stability constants of metal-ion complexes. Spec. Publ. No. 17. Chemical Society, London.

b/ Superscript $^0$ indicates the compound in soluble form.